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CANADIAN ERUCIC ACID OILS

IV. EDIBLE PROPERTIES OF FANWEED (PENNYCRESS) OIL AND SHORTENING¹

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Abstract

Salad oils and shortenings prepared from crude fanweed seed oil by standard methods were lighter in color and more viscous than corresponding commercial products tested, and had slightly lower smoke points. Peroxide oxygen values and free fatty acid contents of all the materials were similar. Small-scale consumer acceptance tests indicated that the fanweed oils, either fresh or aged for 10 days at 100°F., were generally not as palatable as the commercial salad oils (corn and cottonseed), but that the fanweed shortenings did not differ appreciably from the commercial vegetable shortenings. It is concluded that the small amount of fanweed oil present in mixed oil from weed seed screenings will not lessen the potential acceptability of the mixture.

Introduction

The possibility of using Canadian grown rape and mustard seed oils as edible fat sources was suggested in earlier publications (2, 3, 5, 6).

Thlaspi arvense (fanweed, pennycress, French weed, or stinkweed), a member of the Cruciferae (to which rape and members of the mustard family also belong), grows abundantly on the Canadian prairies, and 13% of the weed seed screenings removed from grain crops consists of fanweed seed (4). The oil from such screenings is presently being extracted at Fort William, and uses are being sought for it.

Fanweed seeds contain 33 to 35% oil by weight. The oil is said to be similar in properties to rapeseed oil, and in Russia some consideration has been given to its use as an edible product (1). Consumer reaction to salad oil and shortening prepared from fanweed oil by standard methods therefore appeared to warrant attention.

Materials and Methods

The fanweed seed (300 lb.) used in this investigation was supplied by the Field Crops Commissioner of the Province of Saskatchewan. It was accum-

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ulated from screenings, and contained a small amount of broken flax, and other seeds such as rape, mustard, and lamb's-quarters (total impurities were less than 5%).

The seed was ground in a Hobart mill and the oil extracted in a large all-glass Soxhlet apparatus with petroleum ether (b.p. 85° to 140°F.). Part of the solvent was boiled off, and the rest removed under reduced pressure. The oil obtained was alkali refined, bleached, and deodorized to produce a salad oil; or refined, bleached, hydrogenated to shortening consistency, and then deodorized, as previously described (5, 6). Each test product was a composite of two or three independent preparations. Commercial salad oils (corn and cotton-seed) and vegetable shortenings of good quality were used as reference materials in all tests, and comparisons were made both with fresh oils and shortenings and with oils and shortenings aged for 10 days at 100°F.

Color, fluorescence, kinematic viscosity, peroxide oxygen, free fatty acid, smoke point, melting point, and iodine value were determined for these materials (5, 6). Oils and shortenings were used in the preparation of mayonnaise, pastry, and doughnuts, as in earlier tests (5, 6), except that the amount of oil in the mayonnaise was reduced from about 80% to about 65%. Palatability attributes were scored by a panel of 24 individuals recruited from technical and administrative personnel, on a scale of 11 gradations of appraisal (-5 through zero to +5) ranging from "gross deficiency" through "preferred" to "gross excess".

Results

Characteristics of Oils and Shortenings

The experimental and commercial materials tested were generally similar in melting point and iodine value (Table I). Table II shows chemical and physical characteristics of representative products at various stages of use. The relative light transmissions of the fresh fanweed products were higher than

TABLE I
MELTING POINT AND IODINE VALUE OF TEST SAMPLES

Material	Melting point, °C.	Iodine value
Corn oil	..	122.7
Cottonseed oil	..	114.1
Fanweed oil	..	120.6
Commercial shortening No. 1	38.0	57.4
Commercial shortening No. 2	42.8	66.7
Fanweed shortening No. 1	44.0	64.8
Fanweed shortening No. 2	42.7	71.0

TABLE II
CHEMICAL AND PHYSICAL CHARACTERISTICS OF OILS AND
SHORTENINGS AT VARIOUS STAGES OF USE

Characteristic	Test material	Condition of test material			
		Fresh*	Aged	Fresh, fried	Aged, fried
Light transmission, per cent at 440 m μ relative to mineral oil (Stanolax)	Corn oil	29	27	26	27
	Cottonseed oil	54	55	..	49
	Fanweed oil	65	66	48	46
	Commercial shortening	67	66	50	56
	Fanweed shortening	74	73	37	38
Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol	Corn oil	51	53	47	48
	Cottonseed oil	18	18	..	22
	Fanweed oil	17	17	21	19
	Commercial shortening	18	18	22	22
	Fanweed shortening	14	14	27	27
Viscosity, centistokes at 130°F.	Corn oil	17.0	17.3	17.4	17.7
	Cottonseed oil	17.9	17.9	..	18.8
	Fanweed oil	20.7	20.3	21.1	21.0
	Commercial shortening	23.5	23.7	23.6	23.8
	Fanweed shortening	26.6	26.6	26.8	26.9
Peroxide oxygen value, ml. of 0.002 N thiosulphate per gm.	Corn oil	1.7	1.9	3.2	4.3
	Cottonseed oil	5.6	13.7	..	6.3
	Fanweed oil	0.0	5.4	4.8	6.4
	Commercial shortening	0.0	0.0	2.8	4.9
	Fanweed shortening	0.0	0.0	3.2	5.3
Smoke point, °F.	Corn oil	410	406	408	398
	Cottonseed oil	442	446	..	440
	Fanweed oil	396	383	390	386
	Commercial shortening	419	417	413	405
	Fanweed shortening	388	390	375	390

*The commercial salad oils (corn and cottonseed) and the commercial shortenings were used as purchased and received no further processing.

those of the commercial ones at 440 m μ ; but all values were about 97% at 660 m μ , so these are not presented. Light transmission of all products at 440 m μ was not changed by aging, but decreased with use for deep fat frying of doughnuts. Fluorescence in ultraviolet light (375 m μ) generally increased with frying, except for corn oil, which showed a decrease. The fanweed oil and shortening were more viscous than the corresponding commercial products, and viscosities remained practically constant throughout the experiment. Peroxide oxygen content was zero in the shortenings, increased in the oils on aging, and increased in both the oils and shortenings on frying. Free fatty acid contents,

as per cent oleic, did not exceed 0.2%, so are not shown. The fanweed oil and shortening had lower smoke points than the commercial products and smoke points were generally decreased slightly by both aging and frying. In all these measurements the fanweed oil and shortening did not exhibit any important differences from the corresponding commercial products.

Subjective Appraisals

In two different appraisals of fresh samples, fanweed oil was considered too light in color, and corn oil too dark (Table III). Fanweed oil was rated as

TABLE III
AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS
OF FRESH VEGETABLE OILS

Attribute	Average score		Necessary difference (5% level of statistical significance)	
	Corn oil	Fanweed oil	Between any two av.	Of any one av. from zero
<i>Experiment 1</i>				
Color	+0.6	-1.6	0.8	0.6
Texture	+0.1	0.0	0.6	0.4
Odor	0.0	0.0	0.5	0.4
Flavor	+0.7	+0.3	1.0	0.7
<i>Experiment 2</i>				
Color	+1.1	-1.3	0.5	0.4
Texture	0.0	-0.5	0.4	0.5
Odor	+1.3	-0.1	0.6	0.5
Flavor	+1.5	+1.0	0.7	0.6

slightly lacking in texture in one experiment, although its viscosity was higher than that of corn oil. Corn oil odor was considered too strong in one appraisal. Both fanweed and corn oils were assessed as having a slight excess flavor, but did not differ significantly in this respect. Pastry and doughnuts prepared with fresh oils and shortenings were given generally satisfactory odor scores in two separate experiments (Table IV). Flavor scores were mostly good when the commercial products or fresh fanweed shortening were used, but were relatively poor with fresh fanweed oil.

Aged, independently processed fanweed oils were rated approximately equal in color, texture, and odor to each other and to aged cottonseed oil, but differed in flavor from each other and from the two aged commercial oils (Table V). The attributes of the corn oil were all appraised as "excessive" in varying degrees.

TABLE IV

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF PASTRY AND DOUGHNUTS MADE WITH FRESH VEGETABLE OILS AND SHORTENINGS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn oil	Fanweed oil	Commercial shortening	Fanweed shortening	Between any two av.	Of any one av. from zero
<i>Experiment 1</i>						
Pastry odor	+0.3	+0.4	+0.5	+0.2	0.4	0.3
Pastry flavor	+0.4	+1.0	+0.4	+0.3	0.5	0.4
Doughnut odor	0.0	+0.3	+0.1	0.0	0.2	0.2
Doughnut flavor	0.0	+0.6	+0.1	+0.1	0.3	0.2
<i>Experiment 2</i>						
Pastry odor	+0.1	+0.4	-0.2	-0.6	0.4	0.3
Pastry flavor	+0.5	+2.0	-0.1	-0.8	0.6	0.5
Doughnut odor	+0.3	+0.2	-0.2	+0.4	0.4	0.4
Doughnut flavor	+1.0	+1.2	-0.3	+0.7	0.6	0.6

TABLE V

AVERAGE SCORES RECORDED IN SUBJECTIVE
APPRASIALS OF AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No. 1	Fanweed No. 2	Between any two av.	Of any one av. from zero
Color	+0.9	-0.2	-0.6	-0.4	0.3	0.3
Texture	+0.3	-0.1	-0.4	-0.1	0.3	0.3
Odor	+1.1	-0.3	-0.3	-0.4	0.4	0.4
Flavor	+1.6	-0.1	0.0	+0.7	0.5	0.5

Mayonnaises incorporating the aged fanweed and cottonseed oils were scored as similar in color, texture, and odor (Table VI). Corn oil mayonnaise was rated as slightly in excess in all the attributes under examination. Mayonnaise made with aged fanweed oil had the least satisfactory flavor.

Pastry and doughnuts made with aged fanweed oils were less palatable than those made with the aged commercial oils (Table VII), although excess odor

TABLE VI

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF
MAYONNAISE INCORPORATING AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No. 1	Fanweed No. 2	Between any two av.	Of any one av. from zero
Color	+0.5	+0.1	+0.1	0.0	0.2	0.3
Texture	+0.5	0.0	-0.1	-0.2	0.3	0.4
Odor	+0.6	-0.2	0.0	0.0	0.4	0.4
Flavor	+0.6	0.0	+0.8	+1.0	0.5	0.5

TABLE VII

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF
PASTRY AND DOUGHNUTS MADE WITH AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No. 1	Fanweed No. 2	Between any two av.	Of any one av. from zero
Pastry odor	+0.2	0.0	+0.4	+0.7	0.4	0.4
Pastry flavor	0.0	-0.4	+1.5	+1.7	1.0	0.6
Doughnut odor	+0.3	+0.3	+0.7	+0.5	0.5	0.5
Doughnut flavor	+0.3	0.0	+1.6	+1.0	0.5	0.5

TABLE VIII

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF PASTRY
AND DOUGHNUTS MADE WITH AGED VEGETABLE SHORTENINGS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Commercial No. 1	Commercial No. 2	Fanweed No. 1	Fanweed No. 2	Between any two av.	Of any one av. from zero
Pastry odor	+0.1	-0.2	-0.1	+0.2	0.4	0.3
Pastry flavor	-0.3	-0.1	-0.4	-0.2	0.4	0.4
Doughnut odor	0.0	0.0	0.0	+0.2	0.3	0.3
Doughnut flavor	0.0	-0.1	0.0	+0.2	0.4	0.3

and flavor were found only in slight or moderate amounts. Aged fanweed shortenings, on the other hand, were as acceptable as the corresponding commercial shortenings (Table VIII).

Conclusions

Fanweed oil and shortening processed by standard methods did not differ appreciably from commercial salad oils and vegetable shortenings in most of the chemical and physical properties studied, and the few differences found are not regarded as important. Fanweed oil was generally not as palatable as corn or cottonseed oils, perhaps because of some tendency to flavor reversion, but appraisals of the palatability of fanweed shortening did not differ significantly from those of commercial hardened products. Hence, it is concluded that the small amount of fanweed oil present in mixed oil from weed seed screenings will not lessen the potential acceptability of the mixture.

Acknowledgments

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STOPCOCK LUBRICANTS¹

By J. R. FARNAND² AND I. E. PUDDINGTON²

Abstract

The addition of appropriate quantities of finely divided solids to hydrocarbon, silicone, and glycerol base lubricants has been found to increase their life in stopcocks manyfold. The flow properties of the dispersions show that those solids that materially increase the high shear viscosity, without contributing greatly to the thixotropy of the system, are the most effective. This effect is produced by solids that have a polarity similar to that of liquid vehicle and are readily wetted by the vehicle. Under these conditions, a linear relation exists between the viscosity of the lubricants at a mean rate of shear of 1000 sec.⁻¹ and their life in the stopcock.

Introduction

A major shortcoming of available stopcock lubricants lies in their inability to provide permanent lubrication of the moving parts. Periodic lubrication, especially in low pressure systems, besides being a nuisance is frequently inconvenient and time consuming. While the development of a permanently lubricated, gas tight stopcock would be ideal, formulations that provide increased service life are worth while. The present investigation was initiated to determine what properties are necessary to ensure long service, and to examine means of increasing the life of currently available lubricants. Commercial preparations vary in consistency from very soft greases to heavy plastic solids, and their life in stopcocks is equally variable. Since it seemed probable that a relation existed between consistency and service life, both the flow properties and lubricating value were measured for a number of greases, with rather interesting results.

Experimental

The flow properties of the various lubricants were examined by weighing the amounts extruded in a given time from a steel capillary of 0.1648 cm. inside diameter and 2.545 cm. long. A range of pressures was supplied by compressed nitrogen and suitable reducing valves. The extruder was maintained automatically at a temperature of $30^\circ \pm 0.05^\circ\text{C}$. The apparent viscosity was calculated from Poiseuille's equation and the rate of shear was taken to be $\frac{4v}{\pi r^3 t}$, where the symbols have their usual meaning.

The lubricating values of the greases were determined as follows. The female part of a $\frac{29}{42}$ standard taper ground glass joint was clamped vertically in a block of wood. A length of wire with a 2 kgm. weight attached was passed through the axis and secured to the top of the male part. This provided a uniform

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pressure on the moving member for subsequent experiments. A side arm sealed to the moving part served as a handle. After the joint was lubricated, the handle was turned through 90° and back to its original position. The number of such cycles that could be made before noticeable seizure of the joint or streaking of the lubricant occurred was noted, and the mean of several such determinations was recorded as the lubricating value of that lubricant.

Results and Discussion

Since nearly all the samples examined were thixotropic in some degree, the experimental results were treated to separate the viscous from the thixotropic effects. This was done by plotting the apparent viscosity against the reciprocal of the rate of shear and proceeding as suggested by Goodeve and Whitfield (2).

Typical results for the greases examined are shown in Fig. 1, where a considerable range, both in degrees of thixotropy and viscosity for any rate of shear, will be observed.

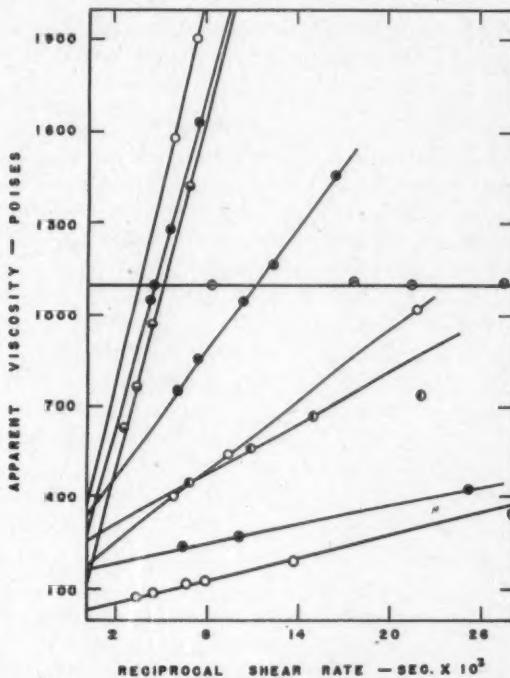


FIG. 1. Typical data for various lubricants. Radial curves in a clockwise direction represent respectively: Dow-Corning lubricant plus 18% silica, hydrocarbon oil plus 25% lithium stearate, Cello-grease, Dow-Corning lubricant plus 10% silica, oil plus 15% lithium stearate, oil plus 25% carbon, Apieson L, and Dow-Corning lubricant. Horizontal curve; glycerol plus 25% silica.

It soon became apparent that the degree of thixotropy of a grease had little bearing on its life in a stopcock and that the lubricating value was due almost entirely to the high shear viscosity. The mean rate of shear in the joint under the conditions used in the experiment was estimated to be about 1000 sec.⁻¹ and the viscosities under this condition were compared with the lubricating value.

In spite of what has been said it is desirable that stopcock lubricants possess a fair degree of thixotropy, since otherwise the lubricant would flow continuously from the joint under the influence of gravity—or atmospheric pressure in the case of a vacuum stopcock. Further, this property is, in general, much less sensitive to temperature changes than is viscosity, and the thinning out that is noted in hot weather with some lubricants can be reduced considerably.

Although the early results indicated that the useful life of a grease in a stopcock was proportional to its high shear viscosity, a few samples were found that gave less service than that predicted. This was found to be due to gel formation, which tended to cause the material to flow through the capillary as a plug or agglomerates, and led to a false viscosity. Milling these samples for some time on an experimental rubber mill, or subjecting them to the high shearing action of a colloid mill prior to extrusion, put them in the predicted position.

Stopcock greases were, until recently, usually thickened hydrocarbons. Pure hydrocarbons having a natural high viscosity are quite satisfactory at room temperatures but, owing to their high temperature coefficient of viscosity, become scarcely usable when a temperature range of a few degrees has been exceeded. For maximum life and usefulness the thickening agent used should be finely divided and contribute only slight thixotropic properties, while adding a large bulk of inert solid to the vehicle. Kruyt and others (3) have shown that this effect is obtained when a solid highly wetted by the vehicle is used. For hydrocarbons an obvious choice is carbon or a very high melting hydrocarbon. Finely divided carbon is available in the form of Shawinigan black and the effect of its addition to a pure hydrocarbon oil having a viscosity of 3500 S.U.S. at 100°F. is shown in Table I. Since the particles adhere to one another tenaciously in the solid state, the carbon black must be added slowly to the oil and the mix well milled during the preparation. Its thixotropic contribution is not high and once a heavy paste has been broken down it recovers but little.

As solids of this sort are not affected by temperature, the viscosity-temperature properties of the liquids are much improved. The vapor pressure of such a preparation is, of course, governed by the liquid used.

Soaps have been used for a long time in the preparation of commercial lubricating greases. Of the soaps, lithium stearate is least affected by temperature changes and its use in conjunction with hydrocarbon oil has been suggested for stopcock lubrication (5). Results obtained with two concentra-

tions of this soap in the same oil as used with Shawinigan Black are shown in Table I. The results again are good. Unfortunately, however, soaps are rather selective in their ability to form stable dispersions in hydrocarbons and this limits their use to those types with which they are compatible.

TABLE I
VISCOSITY AND LUBRICATING VALUE OF GREASES

Grease	Viscosity at 10^3 sec. ⁻¹ rate of shear, poises	Lubricating value, cycles
(1) Dow-Corning	48	338
(2) Dow-Corning plus 10% silica	405	745
(3) Dow-Corning plus 18% silica	590	1200
(4) Glycerine	8 (20°C.)	36
(5) Glycerine plus 15% silica	105	278
(6) Glycerine plus 25% silica	1100	645
(7) Glycerine plus 25% silica (contaminated)	1535	815
(8) Glycerine plus 20% carbon	30	148
(9) Glycerine plus 25% carbon	232	484
(10) Hydrocarbon oil	13.5	119
(11) Oil plus 15% lithium stearate	220	501
(12) Oil plus 25% lithium stearate	465	820
(13) Oil plus 15% carbon	210	380
(14) Oil plus 25% carbon	285	686
(15) Apiezon L	180	460
(16) Cello-seal	242	386
(17) Cello-grease	328	457

For a stopcock lubricant that is comparatively inert to hydrocarbon vapors, glycerine has frequently been suggested (4, 6). Its utility depends on the selection of the proper solid to give the maximum increase in viscosity. Freundlich and Röder (1) showed some time ago that, below the critical concentrations and rates of shear required to produce dilatancy, silica increased the viscosity of water considerably, and hence should be useful for glycerol. Since silica in an extremely finely divided state is now available in the form of aerogels of the Santocel type, it was tried out. Its behaviour in glycerol was similar to that of the carbon black in hydrocarbon and its preparation similar. The effect produced is rather spectacular and is shown in Table I. If pure silica is used in this preparation a liquid with a very high viscosity but no thixotropy is produced; indeed, the system is slightly dilatant.

Since this material possesses no yield value, it tends to flow continuously from the joint. Certain forms of silica, which apparently contained a small amount of impurity, produced systems with glycerine that were somewhat thixotropic. These preparations were very satisfactory lubricants.

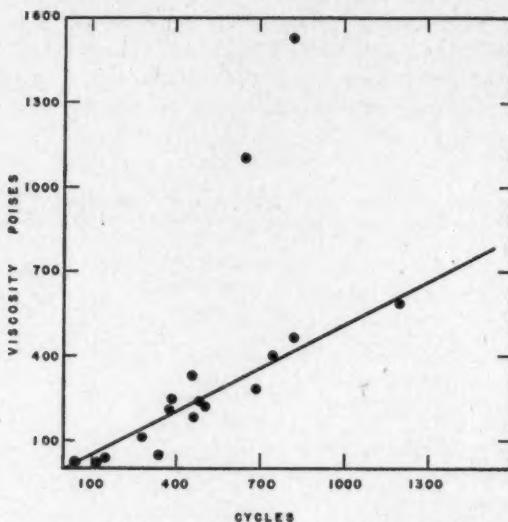


FIG. 2. Variation in service life with high shear viscosity.

The high concentrations of both pure and contaminated silica in glycerine had a service life far less than that predicted from viscosity data. These were the only exceptions (Fig. 2) and no explanation for the behavior can be offered at this time. Two examples are also shown in Table I of quite highly thixotropic systems—carbon black in glycerine. As expected these were inferior to silica.

Low vapor pressure silicone compounds have recently become available as stopcock lubricants. In view of their ability to wet silica an attempt was made to incorporate silica into them in various concentrations. The striking effect on the viscosity and life as a lubricant is shown in the table.

All of the experimental results are summarized in Table I and in Fig. 2, which shows the general linearity in the relation between high shear viscosity and lubricating value. The higher concentrations of solids used here may produce greases that are too viscous for all except very special uses. When using those samples having extremely high viscosity, the stopcocks of necessity are turned slowly.

The results of the work demonstrate feasible improvements that can be made in available lubricants both in temperature resistance and in useful life in the joints and give a possible basis for future developments.

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THE SUSPENDING POWER AND VISCOSITY OF CARRAGEENIN¹

By R. C. ROSE² AND W. H. COOK³

Abstract

This work indicates that the essential factor in suspending cocoa in milk is to increase the viscosity of milk to the point where cocoa does not settle, e.g., 15 centistokes at 10°C. in the system studied. For 21 samples of carrageenin the correlation coefficient between viscosity in milk and suspending power was .98. The high viscosity of cold milk containing as little as 0.04% carrageenin appears to be due to the formation of a casein-carrageenin gel, which is heat sensitive. With 0.1% carrageenin the gel separated into curd and whey when stirred. The correlation coefficient between suspending power in milk and viscosity in 0.05 N sodium chloride was .91; this suggests that the latter could be used to predict the former.

Introduction

Carrageenin, the dried, hot water extract of a red seaweed (*Chondrus crispus*) is used commercially as a suspending agent, particularly for suspending fine cocoa powder in chocolate milk. Little is known about the mechanism of this stabilization and estimates of suspending power are generally based on empirical tests of the minimum amount of carrageenin required to achieve satisfactory suspension of cocoa in milk. This minimum amount ranges, with the different commercial products sold in this country, from 0.04% to 0.08% on the weight of milk. Carrageenin solutions are relatively viscous but the concentrations required to stabilize chocolate milk do not increase the viscosity of aqueous solutions sufficiently to explain suspension by Stoke's law. It appears that the high suspending power of carrageenin can be explained only by postulating a reaction between the carrageenin and one or more of the other components of the system.

Many such reactions are conceivable but the possibility that carrageenin enhances the viscosity of milk far more than it increases the viscosity of aqueous solutions was examined first. Other studies were undertaken to determine the nature of suspension and to correlate suspending power and other physical properties of carrageenin.

Little has been published on physical properties of carrageenin. Salts, particularly potassium salts, enhanced the gelling properties of carrageenin solutions (5, 9). The viscosities of cold water extracts of *Chondrus crispus* have been studied (1, 4) but other work has shown that cold water extracts differ from hot water extracts (5) which are used commercially. The viscosity of carrageenin solutions was decreased by salts (10) and this was explained in terms of decreased solubility, but a more probable explanation is that carrageenin solutions exhibit electroviscous effects and are sensitive to traces of salt.

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Little relation was found between suspending power and the viscosity of 2% solutions at 60°C., or the gold number, or certain other properties (7). The amount of calcium oxalate held in suspension by carrageenin under specific conditions was related to suspending power, but salts affected the results (11). Moreover, colloids often prevent crystal growth and as the calcium oxalate was precipitated *in situ* the prevention of sedimentation may have been due largely to this effect and not to the suspension of particles of the size of powdered cocoa.

Materials

Some samples of carrageenin were laboratory prepared by a procedure described elsewhere (7), others were commercial samples supplied by the Kraft Foods Company and by the Krim-Ko Company. All samples contained salts; salt-free samples were prepared, when needed, by extracting carrageenin with 60% alcohol (by volume) until free from chlorides, then pressing and air drying.

Suspending Power a Function of Viscosity

Methods and Incidental Studies

Solutions of carrageenin were prepared by dispersing carrageenin in milk at 70°C., and holding the mixture, with occasional shaking, in a bath at this temperature for 20 min. They were then cooled rapidly with gentle swirling to 10°C., and stored at 5 to 10°C. for 24 hr. Viscosities were determined in A.S.T.M. Standard, Size 100, Fenske Modified Ostwald Viscometers. Ostwald viscometers are not ideal for thixotropic solutions (such as those encountered in this study) but they have practical advantages. The upper bulbs of the Fenske type of viscometer are filled without running the liquid through the capillary.

Tests showed that concentrations of carrageenin similar to those required to stabilize chocolate milk greatly increased the viscosity of milk and that slightly higher concentrations resulted in the formation of distinct but weak gels. Some difficulty was found in obtaining reproducible viscosities. The milk varied from day to day, so the same milk was used throughout any series. Running the solution through the viscometer reduced the viscosity, therefore the first flow time was recorded; to repeat a reading the viscometer was emptied and refilled with fresh solution. When the solutions containing carrageenin were held at 25°C. their viscosities dropped slowly, consequently a standard warming up time had to be adopted—five minutes was chosen. At 10°C. this warming up problem did not arise and this temperature was used for some of the later measurements. The viscosities of several 0.04 to 0.07% solutions were approximately twice as high at 10°C. as when warmed to 25°C.

A brief study showed that the viscosity developed rapidly in cold milk; immediately after cooling from 70°C. to 10°C., the viscosity of a 0.06% solution of Sample 5 (suspending concentration 0.06%) was 80% of its viscosity

after 24 hr. refrigeration. This is a high initial viscosity, in view of the fact that the solutions are thixotropic and had been swirled during cooling.

The addition of 2% cocoa and 3% sugar, as used in chocolate milk, increased the viscosity of milk and of solutions containing little carrageenin but had no effect on the viscosity of milk containing enough carrageenin to suspend the cocoa. Thus, for 0.05% and 0.06% solutions of Sample 5 (suspending concentration 0.06%), the viscosity at 25°C. in milk was 6.1 and 8.3 centistokes respectively and in chocolate milk it was 6.2 and 8.2 centistokes respectively. Consequently, sugar and cocoa were not included in the main series of viscosity studies.

Chocolate milk suspensions were prepared in the same way as carrageenin solutions, with 2% cocoa (passing 80 mesh) and 3% sugar in addition to the carrageenin and milk. Carrageenin concentrations were chosen at 0.005% increments, e.g., 0.040%, 0.045%, etc. The suspensions were mixed by shaking in stoppered flasks and the mixtures were strained through an 80 mesh sieve prior to refrigerating. Sedimentation was determined visually after storing the mixtures for 24 hr. at 5° to 10°C. The minimum concentration required to stop sedimentation was taken as the suspending concentration, and the reciprocal of this is referred to as the suspending power. Since the determinations were visual and were made at definite concentration increments, the values for suspending concentration are only approximate.

Effects of Carrageenin on the Viscosity of Milk

Fig. 1 shows viscosity concentration curves for five samples of carrageenin in milk. For Sample 1, measurements above 0.04% are not given because above this concentration the milk separated into curd and whey and the viscosity of a 0.045% solution was less than that of a 0.04% solution. Similarly, for Sample 2 the viscosity of a 0.055% solution was less than that of a 0.05% solution.

These curves are all similar in shape and can be made to coincide by selecting a suitable horizontal scale for each one. Thus if the scales for Samples 2, 3, 4, and 5 are divided by the factors 1.12, 1.20, 1.28, and 1.45 respectively the curves all coincide with that for Sample 1. These factors represent the relative concentrations needed to reach a specified viscosity, such as 4, 6, or 8 centistokes. They are referred to in this paper as "relative concentration factors" and the relation among curves as the "relative concentration relation". No special significance is attached to Sample 1 and any of the curves could have been selected as a reference. The factor for an additional sample can be determined by measuring the viscosity of one concentration, say 0.03%, and dividing that concentration by the concentration of the reference sample at the same viscosity. Multiplying the concentration of the reference sample at a selected viscosity by this factor gives the concentration of the additional sample needed to give the same viscosity.

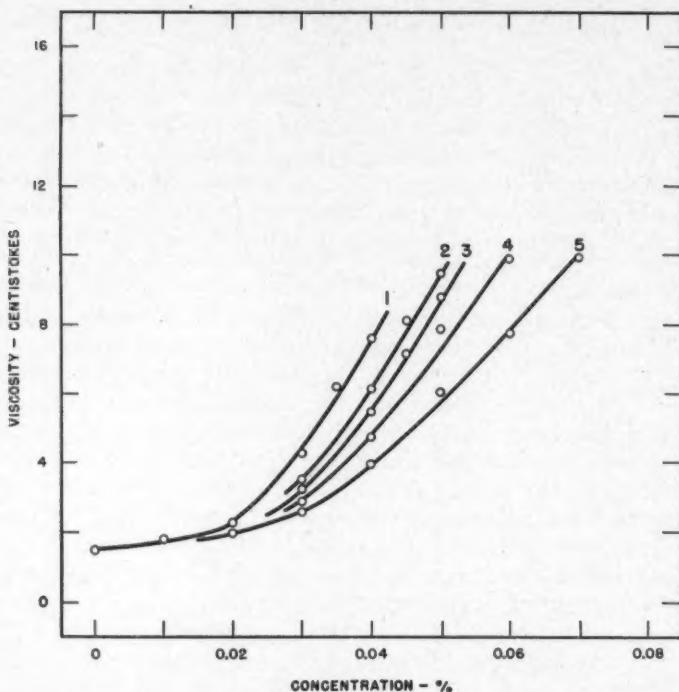


FIG. 1. Effect of concentration on the viscosity at 25°C. of carrageenin in milk.

Relation Between Viscosity in Milk and Suspending Power

For these samples, the suspending concentration was closely related to the amount of each required to increase the viscosity of milk, as measured in this study, to 7.5 centistokes at 25°C., i.e., 15 centistokes at 10°C. To investigate this relation more thoroughly, the suspending concentrations of 16 additional samples were determined and compared with the amount of each required to increase the viscosity of milk to 7.5 centistokes at 25°C. The latter values were calculated from the measured viscosity of duplicate 0.03% solutions of each sample in milk by applying the method given in the foregoing section. A 0.03% concentration of carrageenin was chosen as it gave a good viscosity spread among the samples and the results were more reproducible than those for higher concentrations, which may produce curd and whey.

Fig. 2 shows the results for the 21 samples and the correlation coefficient was .98. The magnitude of this coefficient suggests that stabilizing chocolate milk is a matter of increasing the viscosity to a point where cocoa does not settle.

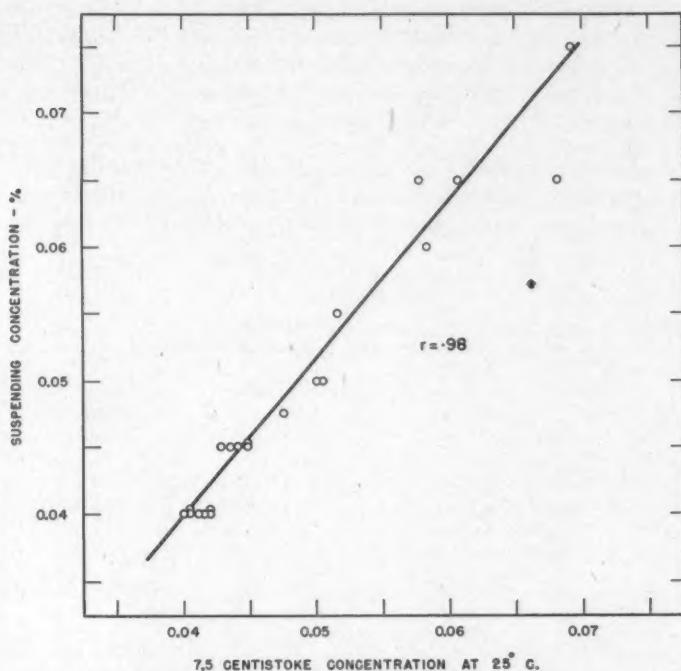


FIG. 2. Relation between suspending concentration and concentration of solutions with viscosities of 7.5 centistokes at 25°C.

Stabilization of Other Systems

If the foregoing is correct it should be possible to stabilize other systems by increasing their viscosities. To investigate this, systems were studied in which the components of chocolate milk were eliminated singly. The methods followed were the same as those used in preparing and studying chocolate milk; care was taken to keep the pigment in suspension until the solutions thickened.

In the first series, pigments other than cocoa were used. Preliminary observations showed that of a calcium carbonate, a talc, a kaolin, and a carbon black, only the last had approximately the same sedimentation rate as cocoa in milk; 2% carbon black on the weight of milk was used. In the second series a low viscosity sodium alginate (obtained from Alginate Industries Ltd., London, England) was used in place of carrageenin. Sodium alginate does not dissolve readily in milk; concentrated aqueous solutions were prepared and one part used to nine of hot milk. Alginate thickens milk because the calcium in milk converts it to calcium alginate, which is a gel under these conditions. In the third series 0.04 N potassium chloride solutions were used in place of milk. Difficulty was experienced in detecting sedimentation in this medium.

In milk, settled particles of cocoa are seen against a whitish background but in aqueous media the background is the same color as the cocoa. This difficulty was diminished by lowering a Lucite rod, with a light at the top, into the medium. Particles could be seen against this light; sedimented particles could be pushed together with the Lucite rod.

The minimum concentration of suspending agents and the viscosities of the stabilized systems are given in Table I. Viscosity is particularly sensitive to concentration in this region, but suspending concentrations cannot be deter-

TABLE I
VISCOSITY OF STABILIZED SYSTEMS AT 10°C.

System	Minimum suspending concentration, %	Viscosity of stabilized system, centistokes
Milk-carrageenin-cocoa	0.040	15.0
Milk-carrageenin-carbon black	0.040	15.2
Milk-sodium alginate-cocoa	0.175	17.1
0.04 N KCl-carrageenin-cocoa	0.225	14.2

mined accurately; therefore, these values (14 to 17 centistokes) are considered to be in good agreement. As high viscosity was the one factor common to all four systems, these results support the view that stabilization is a matter of high viscosity.

The Casein Complex and Carrageenin

Although the foregoing indicates that viscosity is important in stabilization, no clue is given as to the components of milk that contribute to the viscosity increases on the addition of carrageenin; various relations were therefore studied.

Effects of Milk Components on the Viscosity of Carrageenin Solutions

Sample 1 (suspending concentration 0.04%) was used throughout and measurements were made of the viscosity of solutions in the following: milk, skim milk, milk dialyzed for four days against 0.05 N sodium chloride at 5°C. in viscose tubes, whey (from rennet coagulated milk), 2.8% casein at pH 6.8 in 0.04 N potassium chloride, salt solutions whose concentrations approximated that of the various cations in milk (2, p. 294), and 0.05 N sodium chloride. The casein had been prepared by acid precipitation at the isoelectric point. All solutions were refrigerated for 24 hr. and the viscosity was calculated from the first flow time through the viscometer.

In Fig. 3, the viscosity at 25°C. was plotted against the concentration of carrageenin. These results show that skim milk is not appreciably different from whole milk, as only slightly more carrageenin was needed to bring the viscosity to the 7.5 centistoke or suspending level. Whey required a concentration of 0.22%, or five times as much, to reach the 7.5 centistoke level; in fact, whey is no better than 0.04 N potassium chloride, a concentration that

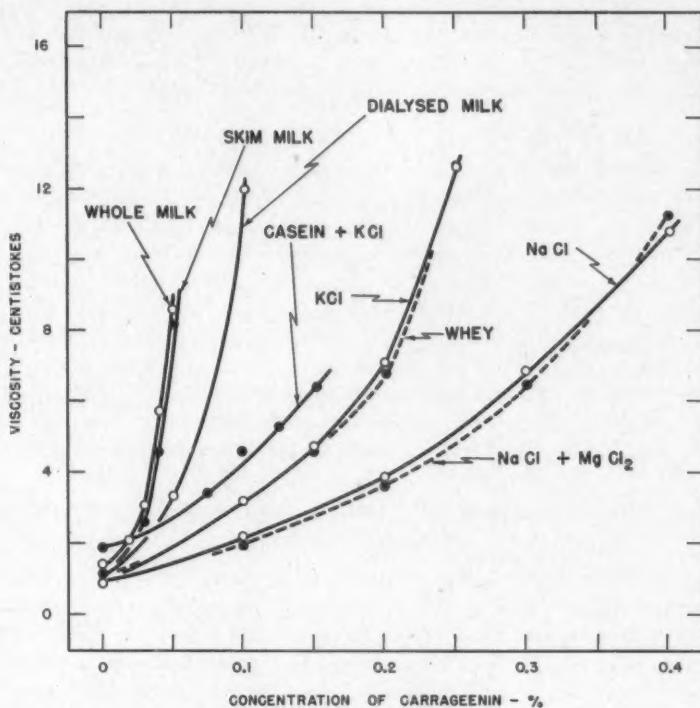


FIG. 3. Effect of carrageenin on the viscosity at 25°C. of milk and milk components.

was selected because milk contains about this amount of potassium ions (2, p. 294). The curves for solutions in 0.05 N sodium chloride and in 0.025 N sodium chloride plus 0.015 N magnesium chloride were similar. The addition of 0.06 N calcium chloride to 0.04 N potassium chloride caused the mixture to separate into two phases and viscosity measurements were meaningless.

The curve for dialyzed milk shows that dialyzing, which probably removed potassium, calcium, and phosphate ions, approximately doubled the amount of carrageenin required to reach the 7.5 centistoke level. Adding potassium chloride to dialyzed milk had no effect. Adding calcium chloride caused the milk to coagulate and it could not be studied.

The curve for casein plus potassium chloride had to be discontinued at 0.15% carrageenin; above this concentration the mixture separated into two phases. The results show that the casein solution did not behave in the same way as milk.

These results show that, with the exception of the removal of fat, modifications of the milk increased the amount of carrageenin needed to reach the 7.5 centistoke level. This suggests that the natural casein-complex present in milk is responsible for the large increase in viscosity of milk on the addition of small amounts of carrageenin. If this complex is upset by dialysis or by removing the casein, much more carrageenin is required to build up the viscosity.

Gelling of Milk with Carrageenin

The most probable explanation of these observations is that carrageenin and the casein-complex gel together. Definite evidence of this was obtained by adding 0.1% of Sample 1 to milk. This set to a gel, which on refrigerating and stirring separated into curd and whey, indistinguishable from rennet curd and whey. An analysis of the whey from the carrageenin-coagulated milk showed it to contain 1.52 mgm. of nitrogen per ml., as compared with 1.42 mgm. of nitrogen per ml. of whey from rennet-coagulated milk. The addition of hydrochloric acid to the whey from carrageenin-coagulated milk did not give a precipitate. These observations suggest that carrageenin effectively precipitated the casein. The casein-carrageenin gel melted when warmed to 40°C., which is in the region of the temperature at which aqueous gels melt.

Relation Between Suspending Power in Milk and Viscosity in 0.05 N Sodium Chloride

Although the foregoing helps to elucidate the mechanism of chocolate milk stabilization it does nothing to explain the difference between carrageenin of high and low suspending powers. As mentioned previously, aqueous solutions of carrageenin are relatively viscous and an obvious choice of investigations was to examine any relation between the viscosity of carrageenin in aqueous solutions and in milk. Before this could be undertaken it was necessary to study the effect of other factors on the viscosity of aqueous carrageenin solutions.

Methods

Aqueous carrageenin solutions were prepared by dispersing carrageenin in boiling water and holding the mixture, with occasional shaking, in a hot water bath for 20 min. The heating time was not critical from the standpoint of viscosity—a solution was heated for an additional 20 min. without reducing its viscosity significantly. For a series of solutions, a stock solution was prepared and diluted by weight with water, salt solution, or buffer, as required, and then heated to 50°C. and cooled again to 25°C. Viscosities were determined in A.S.T.M. Standard, Size 100, Fenske Modified Ostwald Viscometers. pH was determined electrometrically.

Effects of Salts, pH, Storage Temperature, and Concentration

As would be expected these four factors are interrelated. Fig. 4 shows the effects of sodium chloride and of calcium chloride on the viscosity at 25°C. of solutions of 0.1% salt-free, air-dry carrageenin. Curves for magnesium chloride and lithium chloride were similar to those in Fig. 4. It is evident from the shape of these curves that carrageenin exhibits the well known electroviscous

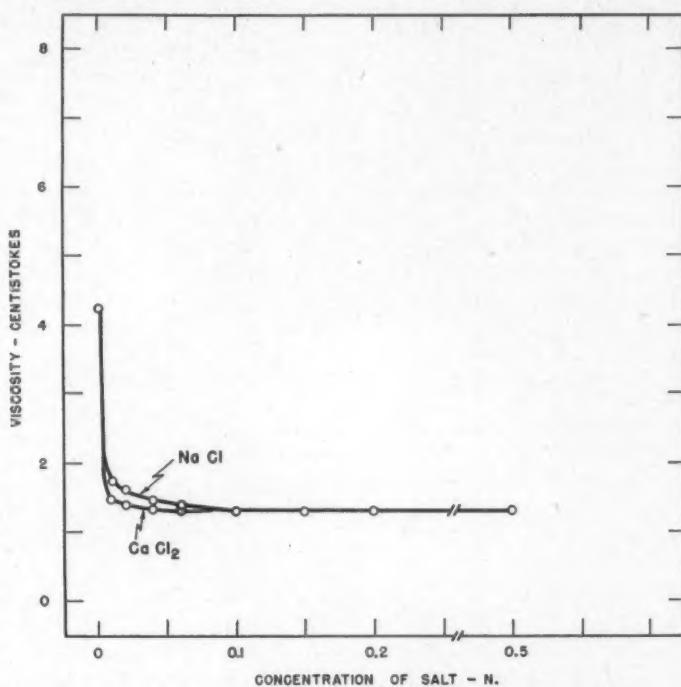


FIG. 4. Effect of salts on the viscosity at 25°C. of 0.1% carrageenin solutions.

effect (6, p. 171). The viscosities of these solutions did not alter over a period of three days at 25°C. Potassium chloride in concentrations up to 0.05 N had the same effect as sodium chloride on the viscosity of 0.1% carrageenin solutions stored at 25°C. but greater amounts of potassium chloride promoted gelling. At 60°C., which is above the gelling temperature of carrageenin, the viscosity of 0.1% carrageenin solution in water was 1.9 centistokes, in 0.1 N sodium chloride it was 0.73 centistokes, and in 0.1 N potassium chloride it was 0.75 centistokes.

Table II shows the effects of pH on the viscosity of 0.1% carrageenin solutions in 0.1 N sodium chloride, after storage at 25°C. for periods up to one week. The solutions were prepared in 0.1 N sodium chloride because preliminary tests

TABLE II
EFFECT OF pH ON VISCOSITY OF 0.1% CARRAGEENIN
(IN 0.1 N SODIUM CHLORIDE) STORED AT 25°C.

pH	Viscosity at 25°C., centistokes		
	After $\frac{1}{2}$ hr.	After 1 day	After 1 week
1.2	1.32	1.03	0.96
3.7	1.36	1.35	1.30
4.4-8.8	1.35	1.34	1.34
12.2	1.34	1.27	1.24

showed that some of the buffers (acetic and boric acid) did not swamp the electroviscous effect. The pH was adjusted by adding 0.1 N hydrochloric acid; 0.1 N mono- and disodium phosphate; 0.2 M boric acid and sodium borate; and 0.1 N sodium hydroxide. The results indicate that hydrogen ion concentration had no appreciable effect except at the extremes, where it probably promotes depolymerization.

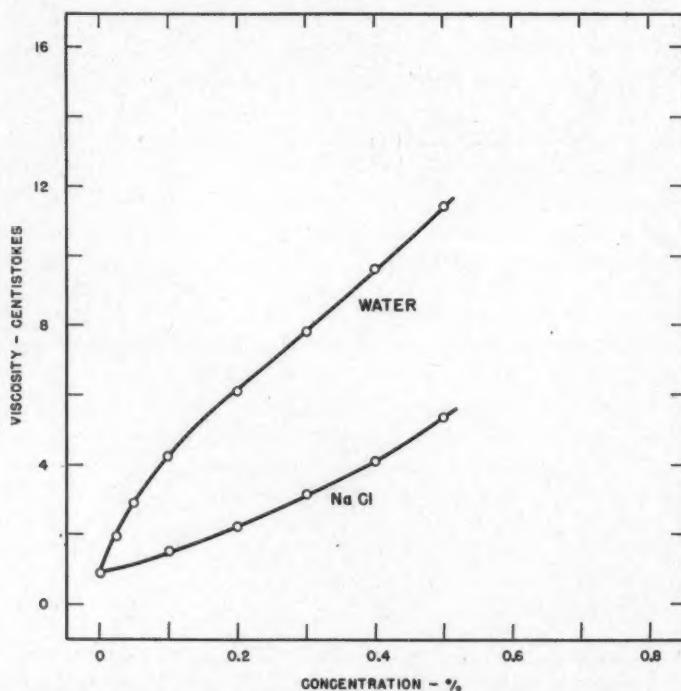


FIG. 5. Effect of concentration and salt on the viscosity at 25°C. of carrageenin solutions.

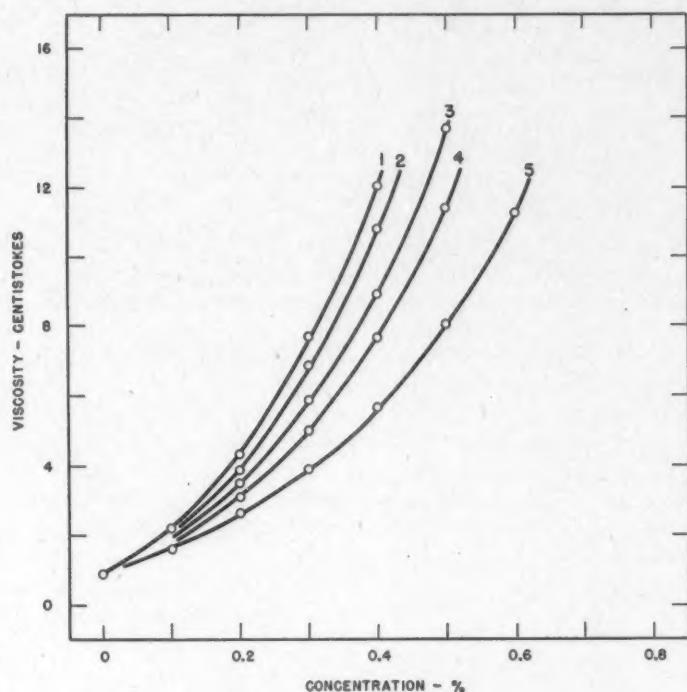


FIG. 6. Effect of concentration on the viscosity at 25°C. of carrageenin in 0.05 N sodium chloride.

Storage at 10°C. increased the viscosities at 25°C. of many carrageenin solutions. This is undoubtedly associated with gelling and may be attributed to aggregation of carrageenin. Salt-free carrageenin gels melted between 35°C. and 40°C. but solutions did not gel unless held at a lower temperature for some time. Gels containing potassium chloride melted between 55°C. and 60°C. Salts that enhanced gelling increased the effect of cold storage on viscosity. A method of avoiding these hysteresis effects is to determine the viscosity at 60°C.

Fig. 5 shows the relation between the concentration of carrageenin and the viscosity of solutions in water and in 0.05 N sodium chloride. None of the solutions had been cooled below 25°C. With low concentrations of carrageenin in water, the viscosity increment decreased with increasing concentration. This is attributed to the autoswamping of the electroviscous effect by the carrageenin itself as its concentration increased.

Fig. 6 shows the viscosity-concentration curves for a number of different samples of carrageenin in 0.05 N sodium chloride. This salt concentration was chosen as it effectively swamped the electroviscous effect but was insufficient to promote gelling in these concentrations of carrageenin at 25°C. These

curves are all similar in shape and the "relative concentration relation" discussed previously holds. If Sample 1 is taken as the reference the "relative concentration factors" for Samples 2, 3, 4, and 5 are 1.08, 1.21, 1.33, and 1.60 respectively. The factors for additional samples, and the concentration needed to give a specified viscosity within the range studied, can be determined as discussed previously.

Viscosity and Suspending Power

Fig. 7 shows the relation between the relative concentration factors for 21 samples of carrageenin in 0.05 N sodium chloride and their suspending concentrations for cocoa in milk; the correlation coefficient was .91. The factors

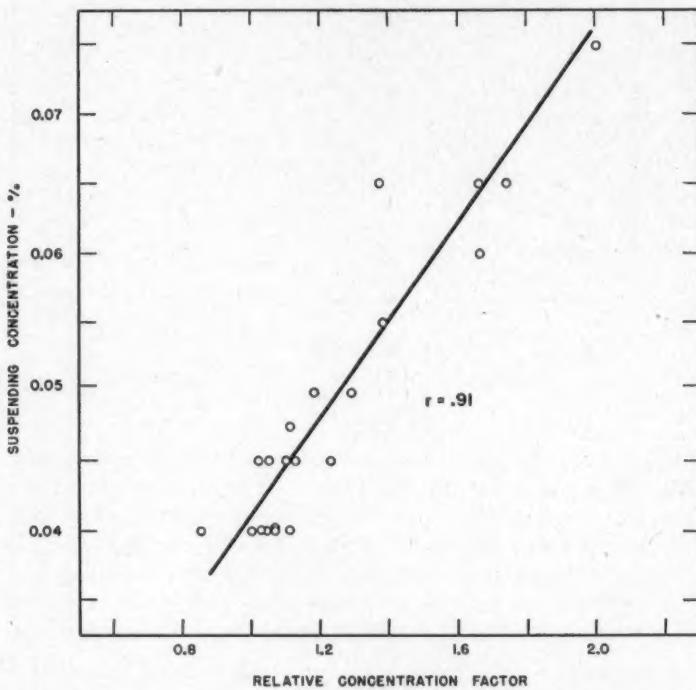


FIG. 7. Relation between suspending concentration and "relative concentration factor" in 0.05 N sodium chloride.

were calculated, as previously described, from the viscosity of duplicate 0.2% solutions. A correlation coefficient of .89 was found between the relative concentration factors in milk and the relative concentration factors in 0.05 N sodium chloride.

The magnitude of these correlation coefficients does not eliminate the possibility that the difference between samples of high and of low suspending

power is due to impurities. An inert diluent in carrageenin would increase its relative concentration factors in both milk and 0.05 *N* sodium chloride proportionately and would not, therefore, affect the relation between them. Potassium salts may enhance viscosity, but a brief study showed that mixing potassium chloride with carrageenin increased its relative concentration factors in both milk and 0.05 *N* sodium chloride in proportion to the amount of potassium chloride added. (The relative concentration factors were calculated from the viscosities at 25°C. of refrigerated 0.03% solutions of the mixtures in milk and freshly prepared 0.2% solutions in 0.05 *N* sodium chloride.) Potassium chloride under these conditions was therefore acting as a diluent.

Extracting a sample of low suspending power with alcohol-water solutions did not increase its suspending power. Storing a sample of high suspending power at 60°C. for 30 days increased its suspending concentration from 0.04% to 0.05%, its 7.5 centistoke concentration in milk from 0.04% to 0.05% and its relative concentration factor in 0.05 *N* sodium chloride from 1.0 to 1.3. These relative increases are similar but in the absence of tests for purity this does not prove that low suspending power is not due to an impurity; the alcohol-water extraction given might not remove impurities and the heat treatment given here and elsewhere (7) could conceivably have modified a portion of the carrageenin so that it constituted an impurity. However, the latter is most unlikely and it appears probable that suspending power is related to the molar mass of the carrageenin.

Summary and Discussion

This work shows that the essential factor in suspending cocoa in milk is to increase the viscosity of milk to a point where cocoa does not settle. With the cocoa used this required a viscosity, as measured in this study, of 7.5 centistokes at 25°C., i.e., 15 centistokes at 10°C. and, since the chocolate milk was stored at the lower temperature, it was the 15 centistoke level that prevented sedimentation. Viscosities were measured at medium rates of shear; at very low rates, such as those caused by slowly settling cocoa particles, the viscosities would be higher. Consequently, the true stabilizing viscosity would be more than 15 centistokes at 10°C. For different samples of carrageenin the correlation coefficient between the suspending concentration and the concentration needed to raise the viscosity of milk to the 7.5 centistoke level was .98. Tests in which the components of chocolate milk (cocoa, carrageenin, and milk) were replaced singly by carbon black, sodium alginate, and 0.04 *N* potassium chloride, respectively, showed that each of the components could be eliminated without upsetting the stability of the system, provided the viscosity was maintained at approximately 15 centistokes or higher.

The results also indicate that the high viscosity of milk containing carrageenin is due to the formation of a casein-carrageenin gel. This gel melts at about the same temperature as an aqueous carrageenin gel, which suggests that the main structure is due to carrageenin. This is supported by the rela-

tion between the viscosity of carrageenin in aqueous solutions and its suspending power. Carrageenin is probably a polymer of a metal-organic-sulphate, linked through the organic part (3), but the gelling of milk with carrageenin is not similar to the precipitation of proteins with detergents, such as sodium dodecyl sulphate, as they precipitate only below the isoelectric point(8).

Probably the carrageenin forms a weak gel into which the casein-complex fits and which it fortifies. It is interesting to compare carrageenin gelling of milk with rennet gelling or coagulation; in the latter the rennet upsets the casein-complex so that it forms an irreversible gel, whereas the former apparently forms a heat reversible gel. The action of carrageenin on the casein-complex may be of use in studying casein.

Finally, suspending power in milk was related to the viscosity of carrageenin in aqueous solutions, and, although this is not in itself proof, it indicates that suspending power is related to the mean molar mass of the carrageenin. This is receiving further study.

From a practical standpoint this work suggests that viscosity of milk containing carrageenin is a reliable measure of its suspending power since the correlation coefficient between them was .98. However, milk itself is variable and unstable and is not an ideal medium for comparative tests. Consequently, viscosity in 0.05 N sodium chloride, although the correlation coefficient between this and suspending power was lower (.91), would probably be a more convenient measure of suspending power. Viscosity in 0.05 N sodium chloride also has the advantage that it can be measured immediately after the solutions are prepared, whereas solutions in milk must be refrigerated for a standard time prior to viscosity determinations.

Acknowledgments

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

X. THE CAUSE OF PREIGNITION (SURFACE IGNITION)— UNDOPED LIQUID FUEL¹

BY R. O. KING² AND E. J. DURAND³

Abstract

The theory is advanced that surface ignition, generally described as preignition, if occurring during compression, is due to partial oxidation of the fuel to aldehyde, a relatively small concentration of this inflammable substance being sufficient for ignition of the charge by the hot surfaces normally present in the combustion space of a high duty engine. The igniting effect may be early or late, that is, before or after spark ignition. Early surface ignition may cause destruction of pistons and exhaust valves of supercharged engines and is indicated by severe knocking. When the effect occurs late in the combustion period there is no destructive effect and the engine will run without spark ignition. The theory is confirmed by engine experiments with rich mixtures which oxidize readily to aldehyde, and it is shown that the occurrence of surface ignition then depends on surface and mixture temperatures. Thus in temperature conditions chosen to eliminate surface ignition, *n*-heptane can be used in the C.F.R. engine at 10:1 compression ratio and the performance of acetaldehyde does not differ from that of a hydrocarbon fuel. A conclusion of importance in practice is that early surface ignition may occur in a particular cylinder of a multicylinder supercharged engine receiving an extremely rich mixture, because of uneven distribution. If the surface ignition led to the destruction of an exhaust valve or a piston, continued running of a highly supercharged engine on the unaffected cylinders would have the disastrous consequences arising from explosion of the compressed mixture in the induction system.

Introduction

An essential condition of the type of knocking combustion frequently described as "detonation" is that the end gas be in a chemical or physical state such that flame propagation can occur in it at an abnormally high rate, otherwise combustion, already proceeding at normal velocity, would be completed without knock. It is held generally that the presensitization of the end gas is due to preflame oxidation reactions. On the other hand, according to the hypothesis advanced in Part IV (10), an abnormally high rate of flame propagation is a consequence of the end gas having become impregnated with finely divided carbon. The carbon is provided by pyrolysis of the lubricating oil when hydrogen or town gas is used as engine fuel, as demonstrated experimentally, Parts V (13) and VI (14), but mainly by pyrolysis of the fuel when liquid hydrocarbons are used.

Abnormally rapid combustion of the presensitized end gas might occur by sudden acceleration of the normal rate of flame movement as in long tubes; in the

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engine combustion space the effect can be initiated by nuclei acting as promoters of ignition or by the igniting effect of hot surfaces. Both types of ignition are shown by the high speed photographs of knocking combustion taken by Withrow and Rassweiler (21). The phenomena are shown even more distinctly by the ultra high speed photographs taken by Miller (17) and by Miller, Olsen, Logan, and Osterstrom (18).

Surface ignition, unlike the nuclear type, need not be confined to the end gas and may occur at any time after the opening of the inlet valve and is described loosely as preignition. The term would better be applied to induction ignition which seldom occurs unless initiated by the residual flame of slow burning mixtures. The term "surface ignition" is therefore applied to an igniting effect arising after the closing of the inlet valve.

When surface ignition occurs before optimum ignition timing, it is equivalent to advancing the spark and will be described as "early". When it occurs after optimum ignition timing, it is equivalent to retarding the spark and will be described as "late". The engine will continue to run on late surface ignition when spark ignition is switched off.

"Preignition" is commonly believed to be due to the igniting effect of incandescent spark plug points or patches of carbonaceous or other matter in respect of the combustible mixture as admitted to the engine cylinder. Induction ignition is possible accordingly but not the surface ignition which occurs especially when using rich mixtures after the inlet valve closes and the "hot points" have been cooled by the entering charge. Incidentally, methanol is exceptionally prone to surface ignition in spite of the cooling effect due to the high latent heat of vaporization. Thus an increase in the inflammability of the combustible mixture during compression in combination with suitable temperatures appeared to be required for promotion of surface ignition.

An increase of inflammability would be obtained on the partial oxidation of the hydrocarbon fuel to aldehyde which is known to occur during compression, and whether or not ignition then occurred would depend on the concentration of aldehyde attained and on maximum surface temperature which can be controlled, especially in a liquid cooled engine. The engine experiments to be described were planned accordingly, it being assumed as indicated by the experiments of Part II (8) that aldehyde is formed by a heterogeneous oxidation reaction and that ignition of the substance is not autocatalytic.

Experimental Arrangements

The standard C.F.R. engine was used for the experiments. Richer mixtures than usual were obtained as required by using oversize fuel flow control orifices. Knock intensity described as "standard" is defined in Part VIII (12, p. 215) and is somewhat lighter than the A.S.T.M. standard.

The fuels used for the experiments were as follows,—

Fuel S, Lot 1: Distillation range 85° to 429°F. See graph of Fig. 1, Part VIII (12), for details.

n-Pentane: technical grade, initial boiling point 94°F., dry point 100°F.

n-Hexane: commercial grade, initial boiling point 150°F., dry point 156°F.

n-Heptane: as supplied for octane number determination according to C.F.R.-A.S.T.M. procedures; boiling point closely approximates the correct value of 98.38°C. (209°F.).

Acetaldehyde: pure, boiling point, 21°C. (70.8°F.).

Preliminary Engine Experiments with the Three Paraffins and Fuel S

Temperatures of initial oxidation or combustion of pentane, hexane, and heptane taken as indicated by the appearance of peroxides, aldehyde, water,

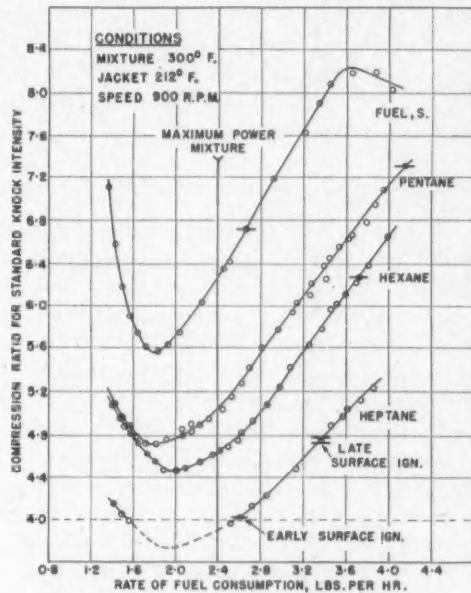


FIG. 1. Effect of mixture enrichment on the combustion of heptane, hexane, pentane and fuel S in the engine.

and carbon oxides in the reaction products, are given by Pye (20, p. 98) as 295°, 266°, and 230°C. respectively. The given values are regarded as approximate only, mixture strength not having been closely controlled.

Preliminary engine experiments using the three paraffins mentioned and fuel S were made in high temperature operating conditions, mixture strength

being continuously enriched to promote surface ignition while compression ratio was increased to maintain standard knock intensity. Ignition timing was retarded as compression ratio was increased, in accordance with the C.F.R.-A.S.T.M. method of knock rating. The results of the experiments are given by the graphs of Fig. 1.

The beginning of early surface ignition is marked on the graphs by single short horizontal lines. It will be noted, as would be expected from the consideration mentioned above, that the effect occurred at decreasing mixture strength and decreasing temperature as represented by usable compression ratio, as the paraffin series was ascended from pentane to heptane.

Late surface ignition on which the engine would run without spark ignition is indicated by the pair of short horizontal lines on the graph for heptane. The effect was obtained with that fuel only. There were indications of early surface ignition when rates of heptane supply were even lower than those indicated on the graph as marking the beginning of the effect. The occasional surface ignition knock then obtained was "heavy", as would be expected. On the other hand, the late surface ignition knock observed when the engine would run without spark ignition was nearly continuous, and intensity differed so little from that adopted as "standard" that it was necessary to switch off the spark ignition to demonstrate the existence of the effect.

Cool Engine Experiments with Heptane

The preliminary experiments indicated that heptane was the most suitable fuel to use for engine experiments to be made in conditions adapted to eliminate combustion knock due to either early or late surface ignition. Further experiments were made, therefore, with the temperature of the jacket cooling water, taken at the outlet, reduced to 100°F., the heptane-air mixture unheated, and the engine speed reduced to 400 r.p.m. to reduce power and consequently the temperature gradient from the combustion space surface to the coolant. The experimental results are given by Graph A of Fig. 2. A second set of experiments was made in similar temperature conditions but with the engine speed raised to 900 r.p.m. The results are given by Graph B of the figure. Graph C of the figure for the heptane as used in standard C.F.R.-A.S.T.M. knock testing conditions is reproduced from Fig. 1 to show the remarkable change in performance obtained on eliminating surface ignition.

There was not the slightest indication of early or late surface ignition during the low temperature experiments, at either 400 or 900 r.p.m. At 400 r.p.m. standard knock intensity could be maintained at compression ratios rising from 4.55 to 10:1 as the rate of heptane supply was increased from 1.3 to 2.1 lb. per hr., which represents an increase in mixture strength of 62%. At 900 r.p.m. standard knock intensity could be maintained as compression ratio was raised from the minimum value of 5.3 to the measurement limit of 10, on increasing mixture strength by 50% only. It should be noted that the minimum

value of usable compression ratio is usually obtained at the "correct" mixture strength and that an increase of as much as 30% may be required to obtain maximum power.

The fuel performance obtained on the elimination of surface ignition is believed to be that governed by nuclear ignition of the end gas, and the de-

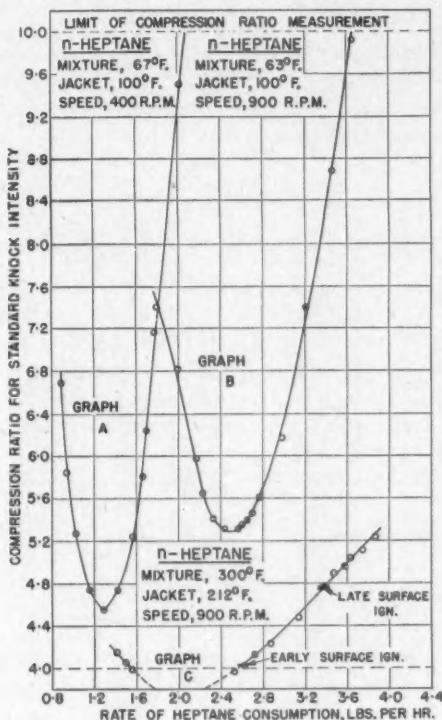


FIG. 2. Effects of surface temperature and enrichment of the mixture on the combustion of heptane in the engine.

crease of knock with increase of engine speed can then be attributed to the consequent decrease in the time available for pyrolysis of the fuel to yield the required concentration of finely divided carbon.

Engine Experiments with Acetaldehyde

Prettre (see W. Jost (7, p. 441)), discussing the luminescence of heated acetaldehyde-air mixtures, mentions that the lively combustion of the mixtures with a small surplus of aldehyde assumes an explosive form that is never observed in hydrocarbon-air mixtures and that normal ignition takes place at about 350°C. Egerton and Gates (2) obtained an igniting temperature of

395°C. on allowing a drop of acetaldehyde to fall into a heated iron pot; the igniting temperature of pentane was 515°C. in the same circumstances. It would be expected, therefore, that an acetaldehyde-air mixture would ignite prematurely if used in an engine as usually operated. Thus Egerton, Smith, and Ubbelohde (3, p. 464) state that the pure substance, b.p. 21°C., when used as fuel for an ethyl knock testing engine was "found to knock so violently that the engine could not be run".

It seemed to be possible, in the light of the experiments made with heptane, that the violent knock observed by Egerton *et al.* was due to early surface ignition and *not* to explosive combustion of the unburned mixture ahead of the flame, late in the combustion period.

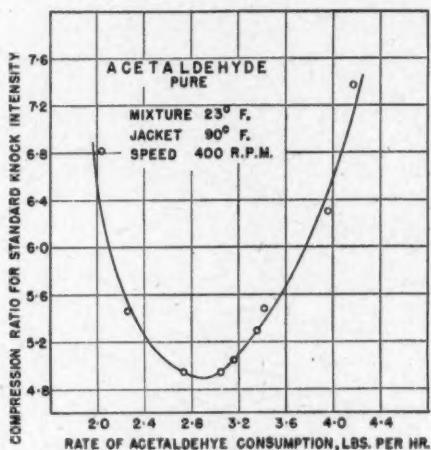


FIG. 3. *The antiknock effect of mixture enrichment when pure acetaldehyde is used as fuel for the C.F.R. engine.*

Experiments with the C.F.R. engine were carried out accordingly in conditions chosen to avoid surface ignition. The jacket cooling water was maintained at 90°F. and the engine run at 400 r.p.m. Furthermore, the experiments were delayed until mid-winter, when it was possible to reduce the laboratory air temperature to 55°F. The quantity of acetaldehyde available for the experiments was insufficient for a determination of the change of optimum ignition timing with change of compression ratio. A fixed ignition advance of 10° was chosen as suitable for a fast burning fuel.

The results of the engine trial are given graphically by Fig. 3. It will be seen that the acetaldehyde behaved like an ordinary hydrocarbon fuel. The minimum compression ratio, 4.9:1, with standard knock intensity was obtained when the rate of aldehyde supply was 2.9 lb. per hr. and standard knock intensity was maintained as rate of supply was increased until compression ratio

reached 7.4:1. The increase of mixture strength was then 48%, the rate of supply of 2.9 lb. per hr. being taken as corresponding to the "correct" mixture strength. The experiment was stopped at the compression ratio of 7.4:1 because frost then affected the flow from the carburetor jet; otherwise it might have been continued until the compression ratio reached the measurement limit of 10:1.

Discussion

The results of the engine experiments accord with the theory that ignition of liquid fuel during compression does not occur until the fuel has been partially oxidized to aldehyde. The results of laboratory experiments described in earlier Parts support the theory.

Thus it was shown by experiments, Part II (8), that pentane ignition temperatures as low as 515°C. and initial oxidation temperatures as low as 295°C. mentioned earlier can be obtained solely if experimental conditions are such that partial oxidation to aldehyde can occur. Turbulence was found to be the essential condition. Oxidation proceeded very slowly without that factor. Reaction was then to steam and carbon dioxide only and, in the absence of aldehyde, ignition could not be obtained even at 750°C., the limit of the indicating instrument. On the other hand, turbulence provided by convection currents in a vertical combustion tube sufficed to start oxidation at temperatures below 300°C., with profuse formation of aldehyde, Fig. 2, Part II, *loc. cit.*, and explosion occurred when the tube wall attained a temperature of 560°C.

The fuel-air mixture on passing the inlet valve of the engine, necessarily with great velocity, enters the hot cylinder and combustion space in a state of high turbulence, and the formation of aldehyde would be expected. The consequent tendency to surface ignition would not, according to the theory advanced, increase with increase of mixture strength unless rate of aldehyde formation increased accordingly. The combined effect of mixture enrichment and turbulence to increase rate of aldehyde formation was shown by experiments described in Part VII (11) using reaction chamber No. 10. The graphs relating to 25% weak, "correct", and 100% rich mixtures with air have been collected and are shown together, Fig. 4 of this Part. Air was supplied to the reaction chamber at 75 cc. per min. and pentane added as required for the stated mixture strengths. The graphs show that aldehyde is formed over the low temperature range at a rate increasing rapidly with increase of mixture strength. The maximum rate of low temperature oxidation, shown by the height of the "aldehyde hump" increased by more than 100% as mixture strength was increased from 25% weak to 100% rich, approximately the usable range in an engine. The fact that ignition did not occur is attributed to the rate of flow through the reaction chamber of 2.5 cc. volume being sufficiently rapid to remove the aldehyde almost immediately after formation.

There is, however, ample available experimental evidence respecting the formation of aldehyde during the compression of hydrocarbon air mixtures in

engines. Thus, Callendar *et al.* (1, p. 28) demonstrated the formation of aldehyde and peroxide during compression and obtained "auto-ignition and detonation" without spark ignition when using a rich mixture of undecane with air in a Ricardo E 35 engine, the mixture being preheated to 80°C. (176°F.) and the jacket water to the same temperature. Measurements were made later by Egerton, Smith, and Ubbelohde, (3, p. 460) of the aldehyde and

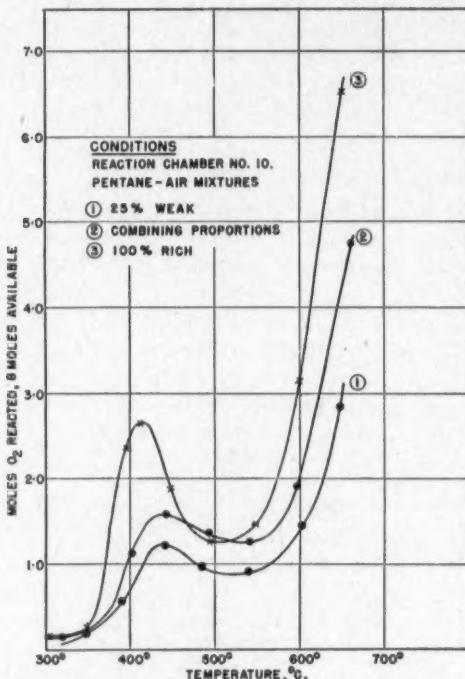


FIG. 4. Oxidation reaction rates over "low" and "high" temperature ranges as affected by increase of mixture strength.

peroxide formed during the compression stroke of an ethyl knock testing engine running at 600 r.p.m., using a jacket temperature 212°F. and unheated induction. Aldehyde was formed up to 10% by weight of the fuel although conditions in respect of mixture strength and temperature were not the most favorable. Moreover, although the engine was run under power, samples for aldehyde estimation were drawn only when spark ignition was switched off.

Concluding Comment

The conclusion arising from the experiments described in this Part, namely, that aldehyde is responsible for the preignition or surface ignition that occurs during compression, is novel, so far as known. The widely held view is that

the effect is due to the premature ignition of the fuel-air mixture, *in the state supplied to the engine*, by exceptionally hot spots in the combustion space such as spark plug points. Temperatures required are, according to Hundere and Bert (6), of the order of 2000°F. (1100°C.) for the first stages of preignition and several hundred degrees higher for very advanced preignition. They conclude that no material in the combustion space can attain the requisite temperatures without melting, other than the ceramic core of the spark plug, certain types of deposits, some from ethyl fluid, because of poor thermal contact with underlying surfaces and in some cases the exhaust valve head. Preignition occurs frequently, nevertheless, in ordinary motor car engines without surface temperatures rising to the degree required to melt an exhaust valve or an aluminum piston.

The usual method of determining preignition temperature is to heat a "temperature plug" projecting into the combustion space until ignition is obtained in advance of the spark. The extremely high "observed" plug temperature would be required unless the mixture contained excess fuel or constituents prone to oxidize to aldehyde. That is, temperatures of 2000°F. and over must have been observed in conditions in which preignition could not occur normally.

The adverse effect of uneven distribution of fuel-air mixtures to multi-cylinder engines, in respect of power developed, has long been recognized. Accurate measurements made by Gerrish and Meem (5) show differences in mixture strength as between cylinders of a multicylinder radial aero engine of as much as 30%, and Marble, Ritter, and Miller (16) describe methods of reducing the differences with the object of increasing the possible maximum power.

The experiments described in this Part show that it is important to provide for uniform distribution in order to avoid surface ignition, which, if occurring "early" in one cylinder of a supercharged engine, may have the disastrous consequences following from the burning of the exhaust valves and piston of that cylinder while the engine continues to run on the others.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. The cost of the work was defrayed in part by an Extramural Grant from the Defence Research Board (Canada). Assistance was given in the course of the work by Messrs. C. C. Li, E. H. Dudgeon, W. E. Morley, and H. W. M. Mar, all members of the staff of the Department of Mechanical Engineering, University of Toronto, and by Mr. H. Shanfield of the staff of the Department of Chemical Engineering.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XI. THE LOSS OF POWER COINCIDENT WITH THE ANTIKNOCK ACTION OF THE CARBONYLS OF IRON AND NICKEL IN RICH MIXTURES¹

By R. O. KING² AND EDWIN J. DURAND³

Abstract

Experiments are described which show that the increase in usable compression ratio obtained on adding iron or nickel carbonyl to rich mixtures with air, of hydrocarbon fuel used in the high temperature conditions of the A.S.T.M.-C.F.R. motor method of knock testing, is not accompanied by a commensurate increase in power. The percentage by which the observed power for the doped fuel is less than that obtainable if a nonknocking fuel were used at the same compression ratio has been determined for various additions of the iron and nickel carbonyls of Fuel S, a commercial gasoline. The loss of possible power when using iron carbonyl in the concentration of 0.50 cc. per liter, increased from 2% at maximum power mixture strength to over 22% at extremely rich mixtures. The loss is attributed to appreciable oxidation of the fuel to final products, prior to the completion of compression, especially when doped fuel is used. Thus the experimental results confirm the theory, advanced in Part III, that metallic antiknocks act by promoting the high temperature surface (heterogeneous) oxidation of hydrocarbon fuel to steam and carbon dioxide; not by inhibiting a homogeneous oxidation reaction by the breaking of reaction chains, as generally supposed.

Introduction

The theories that organic peroxides cause detonation and that the antiknock organometallic compounds act by destroying the peroxides or preventing their formation were first advanced by Callendar and associates (2, 3). The theories in one form or another are still current. Egerton and Gates (5) regard antiknocks "as negative catalysts which react with and remove those substances (peroxides) which auto-catalyse combustion". Egerton in a later publication (4) assumes that preflame oxidation in the engine is a homogeneous reaction, that it proceeds to ignition in the end gas by chain reactions, and that the metallic antiknocks act by breaking the chains. Ubbelohde (15, p. 2943) refers to "the complete inhibition of all oxidation by the addition of antiknocks". Prettre (12, p. 2956) concludes that "the influence of antiknocks in engines can only be explained by their inhibitory action on thermal combustion". Beatty and Edgar (1, p. 2934 and p. 2936) consider that "there is little evidence for the occurrence of significant surface reactions in an engine" and conclude that "antiknock agents act as inhibitors for the slow oxidation in the end gas. Their

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effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

The current theory mentioned above is no longer tenable in view of the experiments described in Parts I (6), II (7), and III (8). They show that the products of *surface oxidation* of engine fuel at *high temperatures* delay the onset of detonation or knocking combustion. The products are steam, carbon dioxide, and carbon monoxide when undoped fuels are used but when the fuel contains metallic dope the products tend to be steam and carbon dioxide only, at any temperature, and the antiknock effect is enhanced accordingly.

The difference between rates of surface oxidation of doped and undoped fuel at high temperatures and the effect of mixture strength on reaction rates were shown by experiments made when using reaction chamber No. 10 and are described in Part VII (10). Rates of reaction were found to increase by 100% on raising the temperature from 600° to 650°C. and to increase by 100% at any temperature within the range, on increasing mixture strength from 25% weak to 100% rich. Nearly 20% of the oxygen in the weak pentane-air mixture passing through the chamber was reacted at 600°C., and 80% of the oxygen in a 100% rich mixture was reacted at 650°C. Similar rates of reaction but at *temperatures 150°C. lower* were obtained when iron carbonyl was added to the pentane.

Temperatures attained by the end gas in an engine when combustion is 90% complete are estimated to be somewhat greater than 650°C. even at the low compression ratio of 4.0 (9, p. 233), and during the whole of the combustion period the "skin" surface temperatures which determine the velocity of surface oxidation would be higher to an unknown degree, because of radiation from the flame. Surface oxidation prior to completion of compression would result in a loss of power. The greater loss would occur if oxidation were promoted to final products by the use of metallic antiknocks, especially as reaction would then proceed at high velocity even at temperatures as low as 430°C. (9, p. 438).

Thus the experiments described in this Part show the *difference* in the effects on power and knock, due to surface oxidation, as between Fuel S and the same fuel containing iron or nickel antiknocks.

Section 1

EXPERIMENTAL ARRANGEMENTS AND RESULTS

The C.F.R. knock testing engine used for the experiments was "standard" except that arrangements were made for accurate measurement of power output.

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for the engine auxiliaries, such as the bouncing pin, the

oil heater, the intake air heater when used, and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, net brake horsepower was measured. Indicated horsepower was obtained by adding, to the B.H.P. observed when the engine was developing power, the brake horsepower required to overcome friction and pumping losses when fuel was not added to the air supply and the engine was "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply.

All the experiments to be discussed were made in the conditions of the C.F.R.-A.S.T.M. motor method of knock testing; mixture temperature, 300°F.; jacket coolant temperature, 212°F.; and engine speed, 900 r.p.m.

Fuel S, Lot 2, a commercial grade of gasoline, generally similar to Fuel S, Lot 1 (11, pp. 212-213), was used for the experiments.

The experimental results are given by the graphs of Figs. 1 to 5. A uniform system of lettering is used. Thus variation of the compression ratio for standard knock intensity with increase of mixture strength is shown for the doped fuel by the *A* graphs and for the undoped fuel by the *A*₁ graphs. The variation of indicated horsepower (I.H.P.) with increase of mixture strength is shown for the doped fuel by the *B* graphs and for the undoped fuel by the *B*₁ graphs.

The term "usable C.R." will be used hereafter as an abbreviation of "compression ratio for standard knock intensity", as defined in Part VIII (9, p. 215).

It is shown by the *A*₁ graphs that the minimum value of the usable C.R. was obtained when the rate of fuel consumption of the undoped fuel was 1.85 lb. per hr., and, as explained in Part IX, it may be assumed that the fuel-air mixture was then approximately "correct" and consequently that percentages by which the mixture strength is rich or weak can be calculated accordingly for other rates of fuel consumption.

NICKEL CARBONYL ADDITIONS TO FUEL S

Concentration: 0.25 cc. per Liter of Nickel Carbonyl. Fig. 1

The graphs of Fig. 1 show that nickel carbonyl in the concentration in the fuel of 0.25 cc. per liter is of slight effect to increase the usable C.R. at correct mixture strength and that there is no increase of power.

Maximum power is obtained at a rate of fuel supply of 2.3 lb. per hr., that is, with a mixture strength 24% rich. The value 4.02 I.H.P. is the same for both fuels within the accuracy of measurement, although the usable C.R. for the doped fuel was 6.5 and for the undoped fuel 6.07. That is, an increase of 0.43 in usable C.R. obtained on adding the nickel carbonyl was not accompanied by any increase of power.

It will be noted that for rates of fuel consumption exceeding 2.5 lb. per hr. the large increases in usable C.R. obtained accordingly were accompanied by relatively large *decreases* in power.

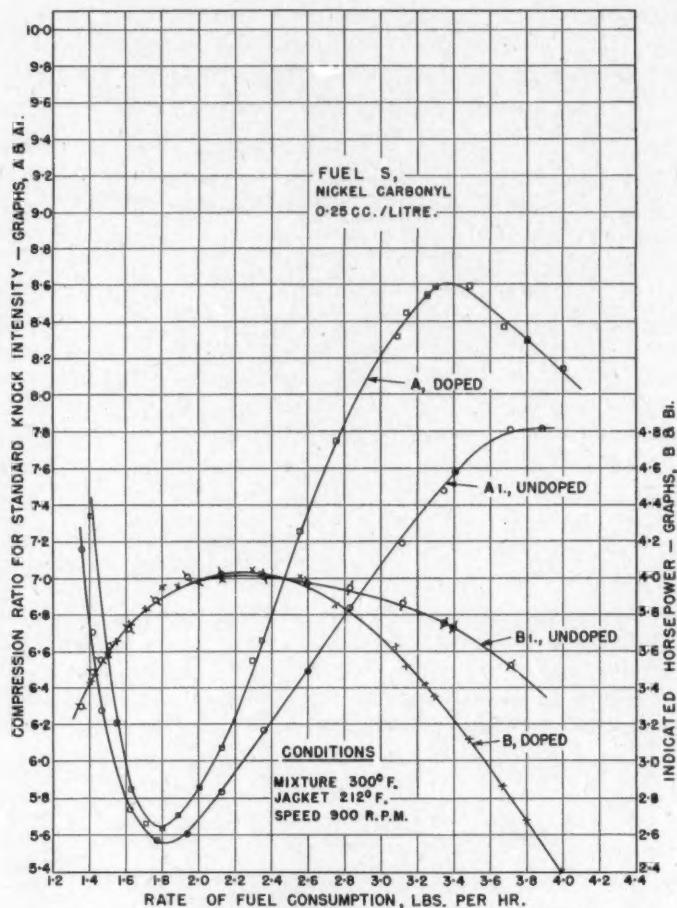


FIG. 1. The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.25 cc. per liter.

Concentration: 0.50 cc. per Liter of Nickel Carbonyl. Fig. 2

The effects on power and usable C.R. are shown in the graphs of Fig. 2. At the maximum power mixture strength, 2.3 lb. of fuel per hr., an increase of from 4.02 to 4.18 I.H.P. is obtained for a usable C.R. increase of from 6.07 to 6.80. The beneficial effect on power diminishes with further increase in mixture strength although usable C.R. increases rapidly, and when rate of fuel

consumption reaches 2.9 lb. per hr. the power developed by the doped mixture at a usable C.R. of 8.34 is the same as that for the undoped fuel at a usable C.R. of 6.92. The mixture strength being still further increased, usable C.R. increases accordingly but the power becomes *less* than for the undoped fuel at very much lower usable compression ratios.

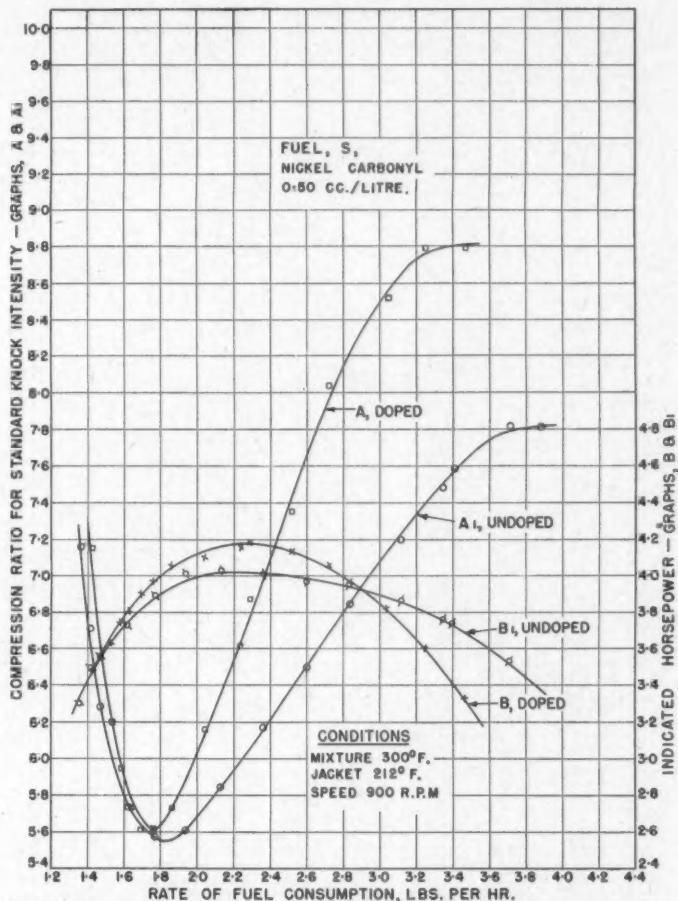


FIG. 2. The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.50 cc. per liter.

Concentration: 1.0 cc. per Liter of Nickel Carbonyl. Fig. 3

The effects on power and usable C.R. are shown by the Graphs of Fig. 3. At the maximum power mixture strength, 2.3 lb. of fuel per hour, I.H.P. increases from 4.02 to 4.34 for the very large increase in usable C.R. of from 6.07 to 7.85.

A usable C.R. of 10, the limiting value for the engine as used, was attained for the doped fuel on increasing the rate of fuel consumption to 2.9 lb. per hr. The increase in usable C.R. from the 6.92 of the undoped fuel was accompanied by an increase of from 3.92 to 4.15 I.H.P., that is, less than 6%.

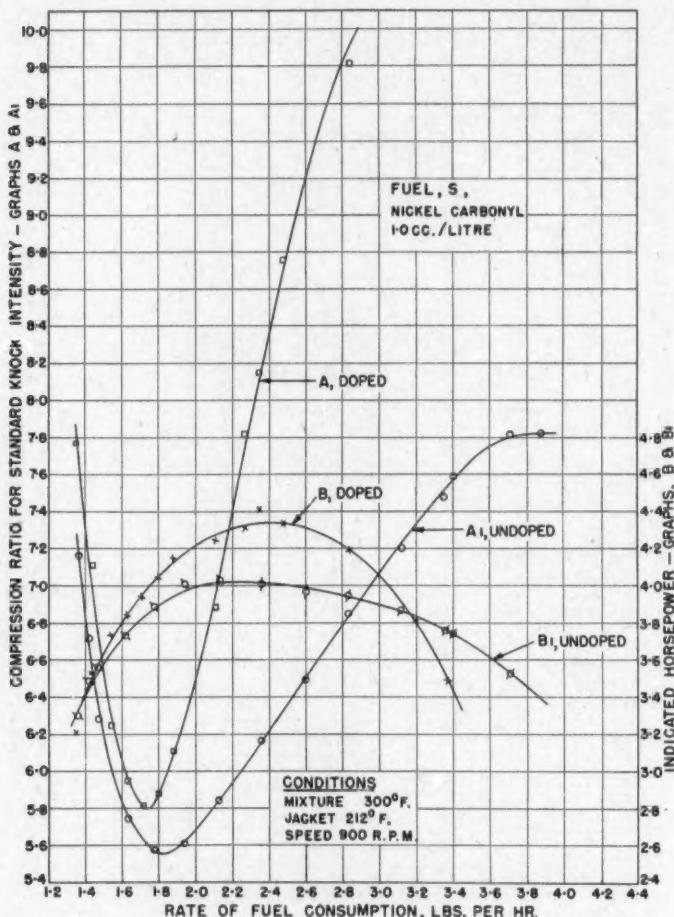


FIG. 3. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 1.0 cc. per liter.*

Equal power was developed by the doped and undoped fuels at a fuel consumption of 3.17 lb. per hr. The usable C.R. for the undoped fuel was then 7.25 but that for the doped fuel was greater than 10.

IRON CARBONYL ADDITIONS TO FUEL S

Concentration: 0.25 cc. per Liter of Iron Carbonyl. Fig. 4

The effects on power and usable C.R. are shown by the graphs of Fig. 4. The antiknock effect of the iron in respect of weak mixtures is noteworthy. Thus the minimum value of the usable C.R. 5.68 was observed when the rate

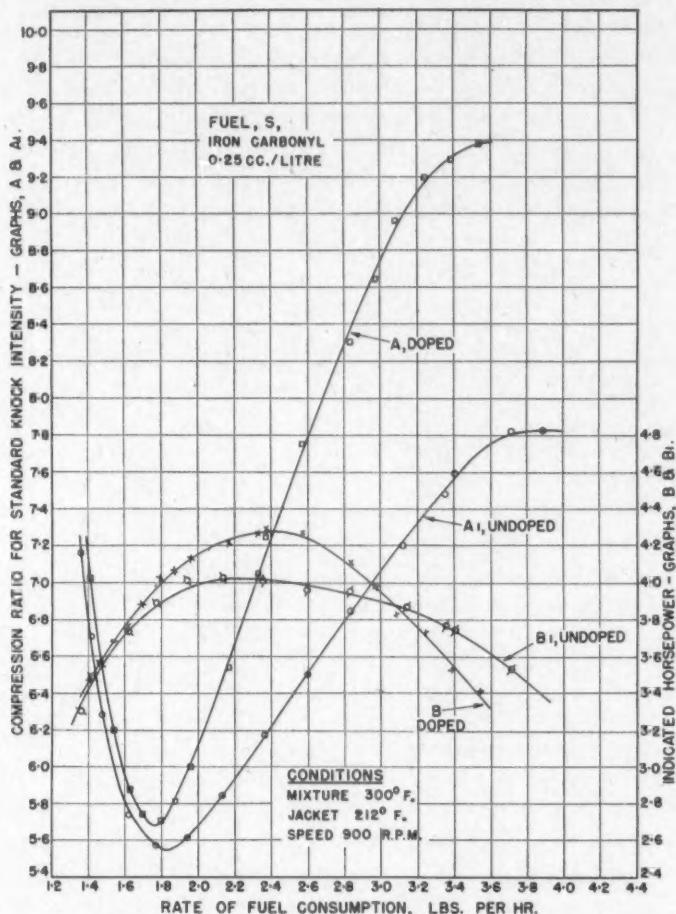


FIG. 4. The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.25 cc. per liter.

of doped fuel consumption was 1.76 lb. per hr., whereas when Fuel S was used undoped, the minimum usable C.R. was 5.54, observed for a rate of fuel consumption of 1.85 lb. per hr. The I.H.P. for the undoped fuel used at 1.85 lb. per hr. was 3.93 and for the doped fuel 4.04 at the same rate of fuel consump-

tion, that is, a power increase of 2.8% was obtained on increasing the usable C.R. from 5.54 to 5.78.

The maximum I.H.P. of 4.28 was obtained for the doped fuel when the rate of fuel consumption was 2.4 lb. per hr.; the usable C.R. being then 7.28. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0; the usable C.R. being then 6.21; that is, a power increase of 7% was obtained on increasing the compression ratio from 6.21 to 7.28.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.1 lb. per hr. although the usable C.R. for the doped fuel was 8.95 as compared with 7.2 for the undoped fuel.

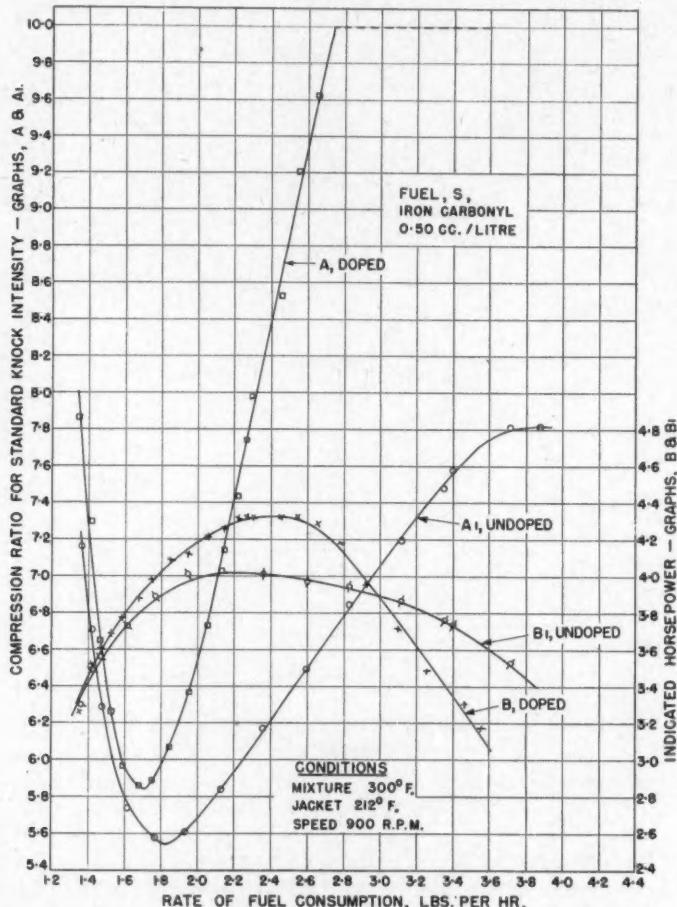


FIG. 5. The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.50 cc. per liter.

Concentration: 0.50 cc. per Liter of Iron Carbonyl. Fig. 5

Considering a rate of fuel supply of 1.85 lb. per hr., usable C.R. increased from 5.54 to 6.07 and I.H.P. from 3.93 to 4.07, that is 3.6% on adding the carbonyl.

The maximum I.H.P. of 4.32 for the doped fuel was obtained for a rate of consumption of 2.4 lb. per hr.; the usable C.R. then being 8.4. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0 and the usable compression ratio 6.21. That is, a power increase of 8% only was obtained on increasing the compression ratio from 6.21 to 8.4.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.0 lb. per hr. The usable compression ratio for the undoped fuel was then 7.06, while the doped fuel was used at a compression ratio of 10, which is lower than the *usable value which could not be determined* because it exceeded the measurement limit.

Section 2

DISCUSSION OF THE EXPERIMENTAL RESULTS

Little if any adverse effect on power would occur if the temperature required for appreciable surface oxidation were attained late in the combustion period, which generally extends beyond top dead center. The required temperature would not, for example, be expected during compression in an unsupercharged engine at moderate compression ratios with the ingoing mixture raised in temperature solely by the usual induction pipe heating.

It has, however, been shown by laboratory experiments mentioned earlier that a fuel such as pentane doped with iron carbonyl and in rich mixtures with air is oxidized to steam and carbon dioxide with high velocity on surfaces at temperatures as low as 430°C. Higher temperatures would be expected during compression, on surfaces in the cylinders of supercharged aircraft engines, and the experimental results of Section (1) support the view that, even in the C.F.R. engine run in A.S.T.M. knock testing conditions, surface temperatures are high enough to cause preflame oxidation sufficient for an easily measurable adverse effect on power, when rich mixtures containing iron or nickel carbonyl are used.

The adverse effect on power, coincident with the antiknock effect of the metallic dopes in rich mixtures used in the C.F.R. engine, has been calculated from the experimental results of Section (1), see Tables I, II, and III below. The calculations require data for the possible percentage increase in power with increase in compression ratio for a nonknocking fuel used at compression ratios extending to 10. The data given by the graph of Fig. 6 are from those compiled by Pye (14, p. 49) for compression ratios of from 4 to 8, and have been extrapolated to a compression ratio of 10. The assumption is made that percentage increase of power with increase of compression ratio as given by the graph of Fig. 6 can be applied generally.

TABLE I
FUEL S PLUS 0.50 CC. IRON CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.8 to 6.95	4.02 to 4.25	5.72	7.93
2.30	24.3	6.07 to 7.9	4.02 to 4.31	7.2	11.8
2.50	35.0	6.36 to 8.85	4.00 to 4.32	8.0	14.2
2.70	46.0	6.65 to 9.8	3.96 to 4.23	6.8	17.5
3.00	62.0	7.07 to +10	3.90 to 3.90	0.0	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.34	-10.5	12.3+

TABLE II
FUEL S PLUS 0.50 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.27	4.02 to 4.16	3.5	3.5
2.30	24.3	6.07 to 6.81	4.02 to 4.18	3.97	4.73
2.50	35.0	6.35 to 7.37	4.00 to 4.13	3.25	6.63
2.70	46.0	6.65 to 7.90	3.96 to 4.05	2.27	7.87
3.00	62.0	7.07 to 8.50	3.90 to 3.84	-1.54	8.23
3.40	84.0	7.57 to 8.80	3.73 to 3.41	-8.6	6.15

TABLE III
FUEL S PLUS 1.0 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.9	4.02 to 4.27	6.2	6.9
2.30	24.3	6.07 to 7.86	4.02 to 4.33	7.7	11.5
2.50	35.0	6.35 to 8.8	4.00 to 4.34	9.2	14.5
2.70	46.0	6.65 to 9.55	3.96 to 4.27	7.8	16.4
3.00	62.0	7.07 to +10	3.90 to 4.05	3.9	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.43	-8.0	12.3+

Thus, with reference to Table I, for example, maximum power, 4.02 I.H.P., was obtained over the range of mixture strength, 18.8 to 24.3% rich. On adding iron carbonyl in the concentration of 0.50 cc. per liter to the richer mixture, usable C.R. could be raised from 6.07 to 7.9. The corresponding increase in

I.H.P. taken from the experimental results, Fig. 5, was 7.2%. If, however, the fuel had been a nonknocking variety, the increasing of the compression ratio from 6.07 to 7.9 would have resulted in an increase of 11.8% in I.H.P. according to the data of Fig. 6. That is, attainment of the higher usable compression ratio by the use of metallic antiknock was accompanied by a loss of 4.6% of the possible increase in I.H.P.

The power obtainable when using rich mixtures of *undoped* fuel may be affected adversely by the enhanced tendency of such mixtures to oxidize on surfaces in the combustion space of the C.F.R. engine when operated in the high temperature conditions of the A.S.T.M. knock testing method. There-

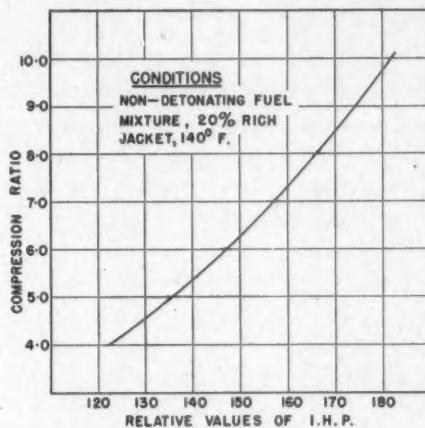


FIG. 6. *The relation between compression ratio and power for a nonknocking fuel used in the Ricardo E 35 engine.*

fore, the experimental results given in this paper are regarded as representing differences in the adverse effect on power of surface oxidation, between Fuel *S* and the same fuel containing iron or nickel antiknock.

Mixture strengths given in the tables range from 18.8 to 84% rich. The maximum I.H.P., Fuel *S*, was constant within the accuracy of measurement over the mixture range 19 to 35% rich and at 84% rich it was 6% only, less than at 2.8% rich. When an engine is run with the compression ratio fixed, it is usually found that power reaches a maximum within the mixture range 10 to 20% rich and diminishes slowly with further increase (13, p. 134). It is to be noted accordingly that values of I.H.P. given in the tables were obtained on increasing compression ratio with increase of mixture strength to maintain a standard knock intensity.

The loss of possible I.H.P. coincident with the antiknock action of the iron and nickel carbonyls is shown by differences between the percentages of Columns 5 and 6 of the tables.

It will be noted by reference to Tables I and II that iron carbonyl in the concentration of 0.50 cc. per liter possesses nearly the same antiknock effect as nickel carbonyl in double the concentration. It will suffice, therefore, to mention the principal features of the experimental results obtained when using iron carbonyl.

The possible loss of power coincident with the antiknock action of iron carbonyl in the concentration of 0.50 cc. per liter, Table I, extends from 2 to nearly 11% as mixture strength is increased from 19% to 46% rich. The loss at 62% rich was greater than 15% and at 84% rich it was greater than 22%. The full extent of the losses at mixture strength greater than 46% rich could not be measured because the compression ratio was then off the scale of the engine when the doped fuel was used.

Concluding Comment

The principal interest of the experimental results lies in their confirmation of the theory, advanced in Part III (8), that the metallic antiknocks act by *promoting* the high temperature surface oxidation of hydrocarbon fuel to steam and carbon dioxide, not by inhibiting a homogeneous oxidation reaction by breaking reaction chains.

Acknowledgments

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THE PREPARATION OF QUINOLINES BY A MODIFIED SKRAUP REACTION¹

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Abstract

It has been found that a modification in the method of bringing together the reactants of Skraup's procedure for synthesizing quinolines results in a marked reduction of the violence of the original reaction and in a substantial increase in yield of quinoline or substituted quinoline. The ease of carrying out the reaction is such that it can be utilized safely and economically on a commercial scale. Examples of the modified method are given for quinoline, 8-hydroxyquinoline, and 5-chloro-8-hydroxyquinoline. The method was applied to the Doebele-von Miller reaction for the synthesis of 8-hydroxyquinaldine and 5-chloro-8-hydroxyquinaldine with somewhat less improvement than in its application to the Skraup reaction.

Discussion

Since the date of its discovery, 1880, the Skraup reaction has been the subject of many researches, the objects of which were to decrease the violence of the reaction and to increase the yields. As originally carried out by Skraup (13) for the preparation of quinoline, the reaction consisted in heating together one part by weight of aniline with one and one-half parts by weight of sulphuric acid and one or more parts of glycerol to 180° to 190°C. The reaction was exceedingly violent in the initial stages and produced a small yield of quinoline. The addition of nitrobenzene to the mixture (14) raised the yield of quinoline to about 50% based on the aniline used.

Subsequent modifications in the process have replaced the nitrobenzene by inorganic oxidizing agents such as arsenic acid (9), picric acid (8), and calcined ferric oxide (1). Recently, the nitrobenzene has been replaced by a small quantity of iodine (7), while the violence of the reaction has been moderated by the use of such reagents as acetic acid (3) and boric acid (4), both of which are believed to form a compound with the glycerol, thereby controlling the amount of free glycerol present in the reaction mixture. Acetylation of the amine (10) has been shown to improve the yield and the ease of operation of the Skraup process.

Modifications in the mode of bringing the reactants together such as adding the sulphuric acid portionwise (5, 11) have not resulted in eliminating the danger of violent reaction and in producing high yields.

It has been observed that the mode of reacting the original Skraup chemicals for the quinoline synthesis is all-important in the matter of control of the vigor

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of the reaction and in the attainment of high yields. The Skraup reactants, namely, glycerol, amine, nitro compound, and sulphuric acid can be mixed with temperature control and then maintained at any convenient temperature up to 120° C. without appreciable chemical reaction taking place. This premix, maintained at a temperature that keeps it fluid (60° to 90°C.), is added in portions to a reaction vessel where each is warmed with stirring to 140° to 170°C. at which temperature the Skraup reaction begins to take place. When the entire mixture has been transferred in this manner, it is heated and stirred under reflux for four to six hours, the end of the reaction being indicated by the disappearance of nitro compound from the reflux liquors. During this time the temperature of the mixture under reflux drops to about 127° to 130°C., owing primarily to the formation of water.

With this procedure, there is no tendency for a violent reaction—in fact heat must be applied continually to maintain the temperature of reaction (135° to 140°C.). It is noteworthy, also, that reaction proceeds at a lower temperature than when other modifications are employed, providing for a smoother reaction and the attainment of higher yields—up to 40% increase. In addition it has been possible to use just sufficient nitro compound so that all of it is consumed in the reaction and there is no need for the recovery of an unused portion.

The principal variables in the reaction have been studied and their most effective adjustment can be described as follows.

1. *Amounts of Reactants*

The effect of variation in the amounts of glycerol and nitro compound employed in relation to the quantity of amine used was studied. In the case of quinoline, it was found that a ratio of from 2 to 2.6 moles of glycerol to one of aniline served to give maximum yields. Lower glycerol-aniline ratios caused a decrease in yield.

For the synthesis of 8-hydroxyquinoline, maximum yields were obtained using a ratio of 3.1 moles of glycerol to 1 mole of *o*-aminophenol. Good yields were maintained with a ratio of 2.7 to 1, but with lower ratios, the yield dropped off. (Table I, Expts. 1 to 8.)

Nitrobenzene or other aromatic nitro compound is used in such quantity as to provide sufficient oxidizing power when the nitro body is completely or almost completely consumed in the reaction. In the case of quinoline, a ratio of 0.535 mole of nitrobenzene to 1 of aniline produced the best yields. Decreasing the ratio to 0.38 to 1 caused a large drop in yield, while increasing it to 0.72 to 1 necessitated the recovery of considerable nitrobenzene. In the case of 8-hydroxyquinoline, a ratio of 0.5 mole of nitro body to 1 mole of amine was found to be the most desirable (Table I, Expts. 9 to 13). However, in the case of 5-chloro-8-hydroxyquinoline somewhat less than the 0.5 to 1 ratio for nitro compound was found to give excellent yields (Expt. 13, Table I).

The use of relatively small quantities of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) gave noticeable improvements in the yields of quinoline as indicated in Expts. 14 to 16, Table I, and had a beneficial effect upon the smoothness of the reaction.

TABLE I
OPTIMUM QUANTITIES OF REACTANTS FOR MODIFIED SKRAUT REACTION

Expt.	Amine (A), gm.	Glycerol (B), gm.	Molar ratio (A) to (B)	Nitro compound (C), gm.	Molar ratio (A) to (C)	H ₂ SO ₄ , gm.	Yield		% yield based on amine
							Gm.	%	
1	Aniline 106	200	1 : 1.9	75	1 : 0.54	364	137	93.1	
2	Aniline 106	220	1 : 2.1	75	1 : 0.54	364	146	90.1	
3	Aniline 106	271	1 : 2.58	75	1 : 0.54	364	146	99.1	
4	<i>o</i> -Amino phenol 56.3	98	1 : 2.1	36.3	1 : 0.5	157	64	85.7	
5	<i>o</i> -Amino phenol 28.2	63	1 : 2.7	18.2	1 : 0.5	79.1	36	96.5	
6	<i>o</i> -Amino phenol 112.6	252	1 : 2.7	72.6	1 : 0.5	314	143.2	96	
7	<i>o</i> -Amino phenol 112	286.8	1 : 3.1	72.6	1 : 0.5	314	154.4	103	
8	<i>o</i> -Amino phenol 28.2	80.5	1 : 3.4	18.2	1 : 0.5	79.1	36	96.5	

TABLE I—Continued

Expt.	Amine (A), gm.	Glycerol (B), gm.	Molar ratio (A) to (B)	Nitro compound (C), gm.	Molar ratio (A) to (C)	Yield		Remarks
						gm.	%	
9	Aniline 106	271	1 : 2.58	50	1 : 0.36	364	112	76.2
10	Aniline 106	271	1 : 2.58	75	1 : 0.54	364	146	99.1
11	Aniline 106	271	1 : 2.58	82	1 : 0.59	364	148	100.5
12	Aniline 106	271	1 : 2.58	100	1 : 0.72	364	145	98.5
13	4-chloro o-amino phenol sulphate 192.6	290	1 : 3.2	86.8	1 : 0.5	260	196	7 gm. nitro compound recovered
14	Aniline 106	271	1 : 2.58	75	1 : 0.54	364	104	70.6
15	Aniline 106	220	1 : 2.1	75	1 : 0.54	364	146	99.1
16	Aniline 106	271	1 : 2.58	75	1 : 0.54	364	148	100.5
								FeSO ₄ omitted
								10 gm. FeSO ₄ added
								20 gm. FeSO ₄ added

2. Combination of Reactants to Form the Premix

The following is the preferred order for combining the reactants. The amine and the glycerol were added to the concentrated sulphuric acid in that order, with cooling, so that the temperature was maintained at 70° to 90°C., the mixture being kept fluid and transferable. The other two reactants, the nitro body and ferrous sulphate, were placed in the reaction vessel ready to be treated, in portions, with the premix.

3. Temperatures

The temperature of the glycerol-sulphuric acid-amine mixture in the case of all the quinolines studied could be raised to 120°C. without reaction proceeding. In the case of quinoline, the temperature during the portionwise addition of the premix was allowed to rise to 160° to 172°C., while during reflux the temperature varied from 150°C. at the beginning to about 135°C. at the end of the reaction. With substituted quinolines, the temperature rarely exceeded 145°C. during the addition of the premix, while during the reflux period the temperature gradually dropped to 129° to 131°C.

4. Rate of Addition of Premix

The glycerol-sulphuric acid-amine premix was added to the reaction vessel at such a rate that the vigor of the reaction produced by each portion had subsided before the next portion was added. However, the procedure described in the paper allows considerable leeway and there is no danger of the violence of the usual Skraup reaction.

5. Stirring

It is preferable to stir the mixture in order to get equal distribution of heat of reaction. However, stirring is not absolutely essential.

6. Time of Reaction

The reaction was complete in four to five hours of heating and stirring following the addition of the last portion of the premix. The end of the reaction was indicated by the disappearance of nitro compound from the reflux liquors.

7. Separation of the Product

In the preparation of quinoline, the base was recovered from the reaction mixture in a good state of purity by a steam distillation. Pure quinoline was obtained by a single distillation. In the case of 8-hydroxyquinoline, the product was isolated from the Skraup reaction mixture, following neutralization, by (1) steam distillation, (2) filtering off the precipitate, drying, and separating the product by vacuum distillation, or (3) precipitating it as the copper (or other metal) salt with control of the pH.

With substituted quinolines, for example 8-hydroxyquinoline, the difficulty is to separate the base from undesirable tarry by-products in a cheap, convenient way. To accomplish this, the neutralized Skraup mixture, which contained the precipitated quinoline and tarry by-products, was treated with suffi-

cient sulphuric acid to dissolve the base and leave the tarry material largely undissolved. The mixture was then stirred at 95° to 100°C. for one-half hour, which treatment served to coagulate the tarry material and facilitate its removal by filtration when the mixture had cooled. This treatment was repeated if necessary, but one such procedure usually served to remove 90% of the undesired material. The acid filtrate was then treated for removal of the 8-hydroxyquinoline as the copper salt.

The pH of the solution has an important effect upon the precipitation of 8-hydroxyquinoline as the copper salt. According to Prodinger (12) copper 8-quinolate is not precipitated below pH 2.2, precipitation is incomplete at pH 2.2. to 2.7, and complete within the range 2.7 to 14. The copper complex precipitates over a wider range than that of any other metal.

The filter cake of copper 8-quinolate normally will contain considerable water which is difficult to remove even on long suction under vacuum. It has been found best to allow most of this water to escape at a fairly low temperature in a current of air rather than try to remove it rapidly at a higher temperature. Thus the filter cake was dried at around 50°C. in a current of air to remove the excess moisture, then pulverized and dried for two hours at 110°C. to remove water of crystallization. The copper salt of 8-hydroxyquinoline is stable to heat at 100°C. for long periods and to sunlight during long exposure.

Experimental

Quinoline

Freshly distilled aniline (106 gm.) and glycerol (220 gm. U.S.P.) were added, in that order, to concentrated sulphuric acid (364 gm.) in a three-liter, three-necked, round-bottomed flask with cooling, so that the temperature was within the range 70° to 90°C. The mixture was then maintained in a fluid state until ready for use by placing it on a steam bath.

The reaction vessel consisted of a three-liter, three-necked, round-bottomed flask fitted with a stirrer, thermometer, and reflux condenser. The flask was charged with a mixture of freshly distilled nitrobenzene (75 gm.) and ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10 gm.), which was heated to 100° to 120°C. with stirring in preparation for receiving the premix of acid, aniline, and glycerol described above.

The premix was then added in about 10 portions to the reaction vessel, reaction being allowed to proceed at 160° to 170°C. before each subsequent portion was added. When all the premix had been transferred to the reaction vessel, the mixture was stirred and refluxed for four hours during which time the temperature gradually dropped to 135° to 140°C.

At the end of the reflux period, the acid mixture was steam distilled to remove any unused nitrobenzene, made alkaline with 50% sodium hydroxide solution, and steam distilled, the heat of neutralization being sufficient to initiate the distillation. The crude product was separated from the aqueous mixture and vacuum distilled, b.p. 109°C. (14 mm.). $n_D^{25} = 1.6232$.

The quinoline produced by this method has a purity of 98 to 99% and contains 0.2 to 0.8% aniline, 0.2 to 0.8% nitrobenzene and a trace of moisture.

8-Hydroxyquinoline

A premix of reactants was made by treating concentrated sulphuric acid (169 cc. 96%) with *o*-aminophenol (112.6 gm.) and glycerol (286.8 gm. U.S.P.) in that order, with cooling and stirring so that the temperature did not exceed 80°C.

o-Nitrophenol (72.6 gm.) and ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10 gm.) were added to the reaction vessel as in the case of quinoline and heated to 100° to 120°C. in readiness to receive portions of the premix.

The amine-glycerol-acid premix was added to the reaction vessel in about 10 portions over two hours, reaction being allowed to proceed at 135° to 150°C. before each subsequent portion was added. The reaction mixture was refluxed for another four hours, during which time the temperature dropped to 129° to 131°C.

(a) *Separation of Product by Distillation.*—The cooled reaction mixture was neutralized with sodium hydroxide (250 gm. in 50% solution) with rapid stirring and addition of pieces of ice so that the temperature did not exceed 40°C. This quantity of alkali was sufficient to bring the solution to pH of about 7 and to cause the precipitation of the hydroxyquinoline, tarry by-products, and some inorganic matter. The entire precipitate was filtered off, air-dried at 50° to 60°C., introduced into a distilling flask with a short Vigreux column, warmed under vacuum to melt the 8-hydroxyquinoline (m.p. 76°C.) and then distilled *in vacuo*. Residual water was first removed and then the 8-hydroxyquinoline collected at 95° to 105°C. (3 mm.) (100° to 110°C. (5 mm.)). The product from such a run weighed 143.2 gm. (the theoretical yield based on amine used is 149.8 gm.) and consisted of a white solid melting at 74° to 75°C.* The hydrochloride, consisting of yellow needles, melted at 234° to 235°C. after recrystallization from methanol-ether. Calc. for $\text{C}_9\text{H}_7\text{NO.HCl}$; C, 59.5; H, 4.41. Found: C, 59.64; H, 4.48.

(b) *Separation of Product as the Copper Salt.* The reaction mixture was neutralized as before. This caused the precipitation of the free quinoline plus a quantity of undesirable tarry by-products. Sufficient concentrated sulphuric acid in 25% solution (42 cc. concentrated sulphuric acid) was added to the mixture to dissolve the hydroxyquinoline. This left the tarry material largely undissolved. The mixture was stirred at 95° to 100°C. for 0.5 hr., which treatment served to coagulate the tarry material and facilitated its removal by filtration from the cooled mixture. The amber-colored filtrate had a pH of 1.5 to 2.5 and was treated with copper sulphate (130 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 25% solution. This caused a further lowering of the pH. The addition of sodium hydroxide (90 gm.) in 50% solution precipitated the copper salt quantitatively

* Melting points are corrected.

from the mixture as a bright green water-insoluble material. It was filtered immediately from the warm solution and washed thoroughly with water to remove inorganic material. The yield of material dried at 110°C. for two hours, after a preliminary drying at 50°C. in a current of air and grinding to a powder, was 190 gm. of 90 to 95% purity. The copper present in the copper 8-quinolate was determined gravimetrically by the method of Berg (2), which consisted of igniting a sample of the copper salt cautiously to cupric oxide in the presence of oxalic acid.

5-Chloro-8-hydroxyquinoline

The method employed for this substituted quinoline was similar to that described for 8-hydroxyquinoline above. The 4-chloro-*o*-aminophenol used was obtained by the reduction of 4-chloro-2-nitrophenol over Raney nickel in methanol, which reduction proceeded quantitatively at 50 lb. pressure of hydrogen and a temperature of 60° in two to three hours. The 4-chloro-*o*-aminophenol was isolated from the methanolic solution as the sulphate salt after filtering off the nickel catalyst, treating with the required quantity of sulphuric acid in methanol, and concentrating to dryness.

The modified Skraup was carried out as described above using 4-chloro-*o*-aminophenol sulphate (192.5 gm., 1 mole) concentrated sulphuric acid (139 cc., 96%), glycerol (290 gm., U.S.P.), 4-chloro-2-nitrophenol (86.75 gm., 0.5 mole) and ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10 gm.). The heating period, following addition of the premix to the reaction flask, was 6.5 hr., the initial temperature being 140° to 150°C. and the final temperature of reflux, 127°C. The completed reaction mixture was steam distilled to remove 7 gm. of unreacted 4-chloro-2-nitrophenol (Table I, Expt. No. 13).

The steam distillation residue was neutralized with 50% sodium hydroxide solution and then made faintly alkaline with sodium carbonate, whereupon the substituted quinoline separated as the free base. The filtered, dried product weighing 248 gm. was dissolved in 5 liters of alcohol and the solution filtered to remove some insoluble black material. The total quantity of by-product tarry material from the reaction was 73 gm. The alcoholic solution was treated with charcoal, boiled, filtered, and concentrated to cause separation of the product as a yellowish-brown crystalline material, weight 196 gm. Yield, 109% based on 4-chloro-2-nitrophenol used for corresponding amine, m.p. 127.5° to 128.5°C. Previously reported values, 130°C. (15), 122° to 123°C. (6). The picrate, consisting of fine yellow needles, recrystallized from methanol melted at 214° to 215°C. Calc. for $\text{C}_9\text{H}_8\text{ON.Cl.C}_6\text{H}_3\text{O}_7\text{N}_3$; C, 44.06; H, 2.2. Found: C, 44.21; H, 2.26.

8-Hydroxyquinaldine

The modified procedure for Skraup's quinoline synthesis, the subject of this paper, was applied to the preparation of 8-hydroxyquinaldine but the yields obtained were no better than when the usual method involving crotonaldehyde was employed. The method follows.

o-Aminophenol (110 gm., 1 mole) was added slowly to dilute sulphuric acid (500 cc., 32%), dissolved, and cooled. Crotonaldehyde (105 gm., 1.5 moles) was then added to the mixture with cooling, so that the temperature did not exceed 30°C. This mixture was run into a flask containing *o*-nitrophenol (70 gm.) over a period of three hours with the temperature at 95° to 100°C. The entire reaction mixture was then stirred for an hour longer at 105°C. Steam distillation of the acid reaction mixture gave 40.5 gm. of unchanged *o*-nitrophenol and caused the separation of about 75 gm. of tarry material from the steam residue. The acid liquor was filtered, made neutral with sodium hydroxide, and then slightly alkaline with sodium carbonate, whereupon the product separated as an orange-brown solid. It was taken up in chloroform, dried, filtered, concentrated, and distilled *in vacuo*. Almost the entire mass of residue came over at 105° to 110°C. (3 mm.) as a colorless to yellow oil. Yield, 111.3 gm. or 70% based upon amine used. On cooling, the product consisted of yellow needles and after recrystallization from methanol melted at 228° to 229°C. (decomp.). Calc. for $C_{10}H_9NO \cdot C_6H_3O_7N_3$: N, 14.43%. Found: N, 14.42%.

5-Chloro-8-hydroxyquinaldine

The above method was applied to the preparation of 5-chloro-8-hydroxy-quinaldine but low yields were obtained. The following reactants were used: 4-chloro-*o*-aminophenol sulphate (77 gm., 0.4 mole), 4-chloro-2-nitrophenol (34.7 gm., 0.2 mole), dilute sulphuric acid (188 cc., 30%), and crotonaldehyde (42 gm., 0.6 mole). The mixture was heated at 90° for 1.5 hr. following addition of reactants and then for a further 1.75 hr. at 100° to 105°C. On steam distillation 24 gm. of 4-chloro-*o*-nitrophenol was obtained. Separation as described above followed by distillation yielded 20 gm. of product boiling at 110° to 120°C. (3 mm.). Theoretical yield based on amine is 77.4 gm. Yield, 25.8%, m.p. 69° to 71°C. The picrate, from methanol, dried at 100°C. for two hours melted at 211° to 212°C. Calc. for $C_{10}H_8NOCl \cdot C_6H_3O_7N_3$; N, 13.25%. Found: N, 13.31%.

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POLAROGRAPHIC DETERMINATION OF THE GAMMA ISOMER OF BENZENEHEXACHLORIDE IN INSECTICIDES AND SOIL¹

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Abstract

A precise and simple method for the determination of the gamma isomer of benzenehexachloride in commercial insecticides and soil by the dropping mercury electrode is outlined. A satisfactory supporting electrolyte consisted of 1% potassium iodide and a trace of gelatin in 50% ethanol.

Introduction

The discovery of the activity of the gamma isomer of benzenehexachloride as an effective insecticide has intensified the need for the development of a simple, rapid, and precise method for its determination. Biological, infrared (2), cryoscopic (1), and partition chromatographic (1) methods have been utilized but are either very time-consuming or require expensive equipment. In recent polarographic studies it was found that only the gamma isomer was reducible at the dropping mercury electrode, and determinations based on this observation have been described (3, 4). The method to be outlined here is less complicated and more satisfactory than the one described by Dragt (3). The modified procedure gave accurate results for estimation of the gamma isomer in synthetic mixtures and in commercial preparations with a variety of carriers and diluents and it also provided a means of estimating recovery from the soil.

Method and Materials

The liquid medium found most suitable to dissolve the benzenehexachloride, the maxima eliminator, and the supporting electrolyte was a 50% solution of ethanol. Methyl red, starch, and gelatin were investigated as maxima suppressors, and, of these, gelatin even in concentrations as low as 0.005% proved the best.

Three indifferent electrolytes were examined; potassium chloride, bromide, and iodide. The first two were not satisfactory, whereas potassium iodide in a concentration of 1% was found to be suitable. Thus the supporting electrolyte consisted of a 50% ethanol solution containing 1% potassium iodide and a few grains of gelatin.

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The diffusion current was proportional to the gamma isomer in the concentration range 10^{-8} to 10^{-5} molar. Below this concentration the accuracy was low, while above it the values started to deviate from linearity. The range found most satisfactory for quantitative determination was between 0.005 and 0.004%.

A cell was constructed that consisted of two compartments, one a calomel electrode connected to the other by means of a salt bridge composed of a fused glass plug and an agar gel saturated with potassium chloride. The other half of the cell contained the test solution into which dipped the capillary. Another capillary was sealed to the bottom of this cell through which hydrogen or nitrogen was passed and through which the test solution was drawn at the end of a determination. The temperature of the cell was maintained at $25 \pm 0.25^\circ\text{C}$. in a water bath. A mercury head of 45 cm. was used while the readings were made with a Sargent model XII instrument.

A sample of suitable size to give a concentration of the gamma isomer within the desired range was dissolved or suspended in the supporting electrolyte. An aliquot of the solution or supernatant liquid was added to the cell, and nitrogen or hydrogen was bubbled through for 20 min. The flow of gas was then stopped and the mercury allowed to start dropping, to prevent plugging of the tip during immersion. The capillary was then lowered into the solution. (A rubber dam surrounding it covered the mouth of the cell and thus excluded oxygen.) This was followed by raising the mercury reservoir to the 45 cm. mark.

Two volts, as read on the voltmeter, was then applied to the system and the current was measured over the range -0.4 to -1.9 v. The current was plotted as an average of the galvanometer oscillations, the wave height measured, and the concentration determined from the calibration curve. The calibration was carried out with known concentrations of the pure gamma isomer by plotting the wave heights against the gamma isomer concentration. Since impurities in the various compounds tested increased the residual current by varying amounts, the whole curve had to be plotted for each sample and the wave height determined by the tangent-intercept method.

The samples assayed that contained the gamma isomer included crude benzenehexachloride containing all the isomers, synthetic mixtures, and commercial preparations with a talc base or added mercury compounds.

The soil samples were extracted with three successive portions of ether, the solvent was evaporated, and the residue dispersed or dissolved in a suitable amount of the supporting electrolyte.

Results and Discussion

The half-wave potential was found to be -1.35 v. and the wave appeared between -0.8 and -1.8 v., all versus the saturated calomel electrode. The dropping mercury electrode possessed an *m* value of 1.39 mgm. per sec. The

drop time was 3.9 sec. at -1.8 v. and 3.8 sec. at -1.0 v. with 0.025% gamma isomer in the electrolyte employed.

Results obtained, using a sensitivity of 50 over a concentration range of 0.04 to 0.01 gm. per 100 ml., are shown in Table I.

TABLE I
WAVE HEIGHT VARIATION WITH GAMMA ISOMER CONCENTRATION

Concentration gamma isomer, %	Wave height in divisions of galvanometer deflection			
	Solution 1		Solution 2	
0.040	52	50	51	50
0.035	45	44	44.5	44.5
0.030	37.5	38	39	38
0.025	31.5	30	31	31
0.020	25	24.5	26	25
0.015	20	19	20	19.5
0.010	11	12	13	12

It was found that the other isomers in the crude material, talc, or mercury compounds that are added to some commercial products had no effect on the wave height for the gamma isomer. In the concentration range 10^{-3} to 10^{-4} molar an accuracy of approximately $\pm 0.5\%$ was obtained. This required averaging several polarographs in order to reduce inaccuracy in plotting, measuring, and averaging galvanometer deflections. A commercial talc base preparation stated to contain 25% of the gamma isomer assayed 24.0% by the above method.

A soil sample that was taken from a plot that had been treated the previous season with gamma isomer at a concentration of 10 lb. per acre and a control sample yielded ether extracts that gave no indication of the presence of any gamma isomer. On the other hand a 25% recovery of the gamma isomer was obtained from a soil sample to which gamma isomer had just been added at the same concentration as to the field sample.

The absence of any gamma isomer in the field sample is not surprising since benzenehexachloride is known to be hydrolyzed, particularly in an alkaline medium and in soils. Recovery of only one-quarter of the recently added isomer is probably due to its partial adsorption. Greater recovery might be obtained by prolonged extraction. However, of significance was the fact that considerable of the gamma isomer could be recovered in the ether extract and determined with no interference from the other ether-soluble material.

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